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TRANSLITERATION

There is no ideal system of translit-
erating Russian; each has its advantages
and disadvantages. For the translation of
Geokhimiya we have chosen the system
used by *Chemical Abstracts*, partly be-
cause of its wide acceptance by other
journals and partly because of certain
advantages in alphabetization of names.
The principal differences between this
system and others in common use are as
follows:

<u>Russian</u>	<u>Chem. Abs.</u>	<u>Others</u>
X	kh	h
И	ts	tz
III	shch	sch
Ю	yu	iu
Я	ya	ia

THE ISOTOPIC COMPOSITION OF OXYGEN IN IGNEOUS ROCKS AND METEORITES

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Abstract

The O^{16}/O^{18} ratio has been determined in stony and iron-stony meteorites, in ultra-basic, basic and acid rocks. The data obtained show that the O^{16}/O^{18} ratio exhibits a tendency to an increased O^{18} content towards acid rocks. The O^{16}/O^{18} ratio values in ultra-basic rocks and meteorites are very similar. Some geological conclusions have been made on this basis.

Several conclusions may be drawn from studies of isotopic ratios of oxygen atoms in igneous rocks of the earth and in meteorites of different types. It is possible, in particular, to make certain suggestions regarding the origin of different kinds of meteorites and of rocks of the earth's crust, based on the progressively increasing dispersion of the isotopic ratios for light atoms (C, O, S, H, etc.) from abyssal ultrabasic rocks to acid rocks, i.e. to granites [1]. The tendency toward increasing dispersion of the isotopic ratios, from ultrabasic to acid rocks, has been indicated for oxygen. Earlier investigators [2] found a difference between the isotopic composition of oxygen in rocks and meteorites. This is easily explainable by the absence, in early years, of mass-spectrometers having sufficient precision to register slight differences in isotopic ratios. However, Baertschi [3] and especially Silverman [4] noted a very slight difference between the isotopic composition of oxygen in some stony meteorites and in granite. It was impossible, nevertheless, to make a comparison between even a small number of data obtained by these investigators, because of differences in the standards they employed as references for the isotopic composition of oxygen of the rocks. Nevertheless they made a joint effort later to reduce their results to one single basis by exchanging their standards [5]. Schwander [6] has studied, in great detail, the O^{16}/O^{18} ratio in the rock series of several intrusions. His results also showed a tendency toward enrichment of O^{18} in acid rocks, as compared to gabbros. However, he reported these variations only on a relative basis.

Because of the inadequacy of such data, it is necessary to obtain supplementary data, if possible, for all types of igneous rocks of the earth. This is the problem which was posed for us. We had also to solve the problem of the choice of the O^{16}/O^{18} standard. It was

decided to adopt the O^{16}/O^{18} ratio in quartz as the standard. This was done because, first of all, the O^{16}/O^{18} ratio in quartz represents a certain extreme, in its high proportion of O^{18} , in comparison with other studied rocks and minerals. Secondly, the oxygen in this standard can be compared easily with any other standard isotopic composition of oxygen. Our choice for the O^{16}/O^{18} standard was completely dry quartz from the Neroika Deposit in Arctic Ural.

Our test materials were iron-stony and stony meteorites (chondrites) from the collection of the Committee on Meteorites, Academy of Sciences of the USSR. The silicate fraction, the olivine chondrites, was separated from the iron-stony meteorites. The light-colored fraction, the least altered one, was taken from the "Saratov" chondrite. The igneous rocks were represented by specimens of their principal types from the collections made by cooperators of the Institute. The dunite specimens were from the massifs of Northern and Arctic Ural and from the northern part of the Siberian Platform. All of the dunite specimens were fresh and unaltered, except the Syum-Keu (item 9 in the Table), which was somewhat serpentized (about 15%). Specimens of fresh basalt were from the Kamchatka Massif and from the craters of Klyuchevskaya Sopka, the eruption of 1938. The granites were from different districts in the Ukraine and had various ages.

In principle the isolation of oxygen is possible, either by the fluoridization of the rock or by its reduction with carbon to CO. We have been using the second method with an excess of pure graphite at a high temperature [7]. Recently we have perfected this method, in the sense of improving the yields of oxygen (as CO), in a short operation at 2100°C in vacuo. Description and verification of the method for the isolation of oxygen from rocks are presented in a separate publication. Numerous tests have shown that in our procedure the yield of oxygen (CO) is practically 99 to 100%. The quartz standard was treated in exactly the same way as the test materials, i.e. it was subjected to the preliminary degassing at about 1000°C and to the reduction by graphite.

The carbon monoxide was freed from its possible impurities, placed in a glass ampule, and attached to the mass-spectrometer for analysis. The isotopic ratios of oxygen were registered by the 28 and the 30 mass (CO^+). Determinations of the O^{16}/O^{18} isotopic ratio were so conducted, in every case, that the differences between the ratios of the standard and of the test material were repeatedly and alternately recorded by an automatic device. The entire mass spectrum was observed during the analysis in order to exclude possible effects of foreign admixtures. The average relative error of a determination did not exceed $\pm 0.02\%$, judging from magnitudes of the differences obtained when replicate samples of the gas were isolated from fresh samples of the same rock. This served to define the reliability of the procedure. The maximum error was as much as $\pm 0.04\%$ in some isolated cases. As shown in the table, the averages were calculated from two or three independent parallel replicate analyses made at different times.

The absolute magnitude of the O^{16}/O^{18} ratio for oxygen in the quartz standard was determined by the same mass-spectrometer. The accuracy of the determinations of the deviations from the standard, 0.02%, represents the reliability of $\pm 0.1\%$ in the determined absolute magnitudes of the O^{16}/O^{18} ratio. This includes corrections for the O^{17} and the C^{13} isotopes and for the discrimination of the apparatus. The absolute magnitude of the O^{16}/O^{18} ratio for quartz was used in the calculations of the absolute O^{16}/O^{18} ratio for oxygen of the rocks. Consequently, the data on the O^{16}/O^{18} for rocks and meteorites here reported are very close to the absolute isotopic proportions. The O^{16}/O^{18} ratio in the CO of the samples was calculated by the equation: $R = R_{st.} (1 - \delta/100)$, where δ is the percentage difference between the isotopic ratio for oxygen in the standard and in the test material, $R_{st.}$ is the O^{16}/O^{18} for the standard, and R is the O^{16}/O^{18} for the test material.

The method of the mass-spectrometric recording of the O^{16}/O^{18} ratios in CO and the method of the determination of the absolute isotopic ratios for oxygen were described in detail, in the previously cited publication.

Examination of our data on the isotopic ratios for oxygen from different meteorites and igneous rocks (see table) shows, first, that there are certain differences between these materials and, second, that there are also differences in the degree of scattering of the isotopic data for different materials. The greatest scattering of the O^{16}/O^{18} ratio is shown by igneous rocks; the least scattering is shown by meteorites, both stony (chondrites) and iron-stony ones. In this latter case, the degree of scattering fluctuates in the vicinity of ± 0.2 . Moreover, it should be noted that the silicate fractions of pallasites, as well as stony meteorites, show an identical O^{16}/O^{18} ratio, which points to their genetic relationship and excludes all of those possible processes of their formation that could have disturbed their O^{16}/O^{18} ratio. It appears that it may be possible, in the future, to suggest that the isotopic composition of oxygen in meteorite-chondrites be used as universal standard in geochemical research.

The regular trend in the O^{16}/O^{18} ratio, from its maximum in the silicate phase of meteorites to its minimum in granites and, finally, quartz, is a subject of cardinal interest. In other words, there is a parallelism between the SiO_2 content, increasing progressively from the silicate phase of meteorites to granites, and the content of O^{18} . Thus the isotopic ratios of oxygen in meteorites and in igneous rocks change in the same direction as the isotopic ratios of other light atoms, has been already indicated.

The silicate phases of meteorites and ultrabasic rocks have very similar oxygen isotopic ratios: O^{16}/O^{18} is about 490.2 ± 0.1 . Minor deviations from this level are already noticeable in some ultrabasic rocks, in dunites and, next, in basalts. The minimum of such departures from the standard is reached in granites: O^{16}/O^{18} about 488.7.

Table 1.

Item	Material	Source	Departure from the standard %	Absolute magnitude of O^{16}/O^{18}	Average O^{16}/O^{18}	Remarks
IRON - STONY METEORITES (PALLASITES)						
1	Pallas iron	Medvedeva Village, Krasnoyarskii Krai, RSFSR. Found in 1794	-0.74 -0.74	490.6 490.6	490.6	Collection of meteorites; Committee on Meteorites, Academy of Sciences of the USSR
2	"Bragin"	Bragin Rayon, Polesskay Oblast, BSSR. Found in 1937	-0.69 -0.70	490.4 490.4	490.4	
3	"Marialahti"	Finland	-0.68 -0.66	490.3 490.2	490.2 ₅	
STONY METEORITES (CHONDRITES)						
4	"Saratov"	Saratov Oblast', RSFSR; fell Sept. 6, 1918	-0.75 -0.72	490.6 490.5	490.5 ₅	"
5	"Zhovtnevyi Khutor"	Khutor Zhovtnevyi, Stalinsk Oblast, UkSSR; fell Oct. 9, 1938	-0.67 -0.67	490.3 490.3	490.3	
Average					490.4	
ULTRABASIC ROCKS						
6	Dunite	Arctic Ural; Syum- Keu (Sample #1005)	-0.78 -0.76 -0.76	490.8 490.7 490.7	490.7	Samples sup- plied by Yu. E. Moldavantzev
7	Dunite	Arctic Ural; Kytlym; Konzhakovskii Kamen	-0.65 -0.72	490.2 490.5	490.3 ₅	
8	Dunite	North of Siberian Platform; Sabyda- Gulinsk Intrusion	-0.60 -0.54	489.9 489.6	489.7 ₅	From E. M. Epstein
9	Dunite	Arctic Ural; Syum- Keu Massif (Sample #1002)	-0.57 -0.56	489.8 489.7	489.7 ₅	From Yu. E. Moldavantzev
10	Dunite	Arctic Ural; Rai-Iz Massif	-0.46 -0.46	489.2 489.2	489.2	From Yu. E. Moldavantzev
Average					490.0	
BASIC ROCKS						
11	Basalt	Kamchatka; Klyuchevskaya Sopka; Kirgurich	-0.48 -0.45	489.3 489.2	489.2 ₅	
12	Basalt	Kamchatka; Klyuchevskaya Sopka; Bilyukai Crater, eruption of 1938	-0.38 -0.37	488.8 488.8	488.8	
13	Basalt	Kamchatka; Tolbachik	-0.70 -0.70	490.4 490.4	490.4	
Average					489.5	

ACID ROCKS						Absolute Age; Vinogradov [8] million years
4	Granite	Ukraine; Karer Podstepnoe	-0.36	488.8	-	1200
5	Granite	Ukraine, Krivorozhe	-0.36	488.8	-	1900
6	Granite	Ukraine; town of Shpola; Prudy- anskii Karer	-0.28	488.4	-	1600
		Average			488.7	
7	Quartz std.	Arctic Ural; Neroika Deposit	-	487 ± 1	-	

It is possible for us therefore to believe that, as the result of the formation of the earth's crust, the substance in the earth's mantle whose composition resembles the silicate phase of meteorites is undergoing alterations which are accompanied particularly by the isotopic exchange of oxygen.

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RADIOACTIVITY OF VARIOUS ROCK COMPLEXES OF THE TERSKEI ALA-TAU MOUNTAINS

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Abstract

The influence of Caledonian granite intrusions on the variations of the radioactivity of the earth crust area in Tyan-Shan has been considered. Several thousands of rock specimens of various complexes have been analysed for U, Th and K. The total chemical compositions of rocks of various complexes are given.

The principal conclusions are the following: during the formation of granitic batholiths (in the case of replacement of host rocks) radioactive elements (U, Th, K) are carried in to an essential extent together with silicon and alkalis. At the same time calcium and magnesium are carried out in considerable quantities, and to a lesser degree, iron, manganese and titanium. This tendency grows in the second phase granites, which represent the further development of the magmatic process.

Granitic intrusions play an important role in the problem of the distribution of radioactive elements in different shells of the earth and in different parts of the earth's crust. It has been established that granites are the most highly radioactive rocks. It appears, therefore, that there is a certain irreversible process resulting in the accession of radioactive elements from the depths to the crust of the earth. This circumstance must lead to results of a most diverse character. The most important of these is the change in the distribution of energy in different layers of the earth resulting in tectonic adjustments and in an intensification of magmatic processes. These theses were stated clearly and consistently in the publications of V. V. Belousov [1].

It should be interesting, therefore, in such connections, to follow through the sequence of changes in the average abundance of radioactive elements (in relation to chemistry of the rocks), as influenced by granitic intrusions, in different parts of the earth's crust. This may also help, to some extent, in the clarification of certain controversies on the origin of granites.

Studies of this kind may have also a wider geochemical significance, inasmuch as radioactive elements play a special part in widely different fields of geology. We had chosen as the subject of the present study an extensive area in Central and Northern Tyan-Shan, where the Caledonian intrusive activities are very strongly represented.

So far only the Terskei Ala-Tau materials, representing a fairly large territory (12,000 km²), have been prepared for the report. This geologic structure is an immense anticlinorium which includes a very large intrusion of Caledonian porphyry type granites and granodiorites (a²) of the batholithic type. There are relatively small bodies of Caledonian alaskite granites of the Second Phase (γ_2^3) in the marginal parts of the intrusion. Proterozoic and Hartz granites are not abundant in the territory here described. The area of their exposures amounts only to a few per cent of the area of the exposed Caledonian granitoids. These granites have certain characteristic features. The Proterozoic ones contain relatively small amounts of radioactive elements (less than in the Caledonian granites), whereas the Hartz granites contain more of them than the Caledonian granites [3]. This is an interesting fact in our studies of the changes in the content of U and Th of granitoids belonging to different cycles of intrusive activity. However, we consider granites as the source of major variations in the content of radioactive elements in the rocks of the subsequent formations, while referring the chemistry of the granites themselves to the host rocks,* within the area of our study.

In the plan of the report here adopted, rocks of the metamorphic series (including the Silurian and the still more ancient sediments) are very important, as the host rocks of the Caledonian intrusions; Cenozoic sediments are also important, as they were formed after a partial water-erosion of the granitoids.

Carboniferous and Jurassic sediments are relatively scarce in our area. They are represented by their own characteristic facies, and they are composed chiefly of materials originating outside the area. Because of that, these sediments are not considered in the present study dealing with the analysis of a small part of the Tyan-Shan. We are reporting, therefore, the results on the radioactive elements only in the three major complexes of the rocks, namely:

1. Proterozoic and Lower Paleozoic metamorphic rocks, which are the host rocks of the Caledonian intrusions and which are apparently assimilated or replaced by them, to a certain extent.
2. Caledonian granitoid intrusions which are responsible for the fundamental geochemical alterations of this particular section of the earth's crust (they occupy more than 50% of the area of Central Tyan-Shan).
3. Cenozoic sediments representing a rejuvenation in the composition of the rocks caused by the intrusive activity. Cenozoic rocks are abundant in the Issyk-Kul Lake Basin where they are represented by thick beds of local materials.

This paragraph means: "However, the Proterozoic and the Hartz granites cannot be regarded important as sources of large amounts of radioactive elements in the later formations, if we assume that granites are major sources of radioactive elements, as a rule, and if we consider the chemical composition of our granites in reference to the chemical composition of the rocks invaded by them, within the boundaries of the areas of study." VPS

We must say a few words now about the Caledonian granitic intrusives.

The First Caledonian Intrusion of Granites and Granitoids, (γ_2^2).

This is a gigantic intrusive body forming the entire axial part of the Terskei Ala-Tau Range (about 300 km long).

Gray porphyry-type granite commonly grading into granodiorites are the predominant rocks of the intrusion. Dark minerals are abundant in the rocks. There are many zoned plagioclases. There are pegmatitic and aplitic dikes in the granites. Schlieren and xenoliths (locally regularly oriented) are commonly found. Hybrid rocks of the diorite type are present locally on the margins of the intrusive.

A general impression is to the effect that a replacement of the host rocks played a major role during the stabilization of the intrusion. This is only natural, if we take into account the gigantic size, the complexity of the composition, and the configuration of the intrusive body.

The age of the granites is about 340 million years, as determined by the argon method [4].

The Second Caledonian Intrusion of Leucocratic Granites (γ_2^3).

These granites are markedly less abundant than the granites of the First Intrusion (the area of their outcrops is less than 10% of the outcrop area of the First Intrusion granitoids), but they are highly varied, are close to the granites of the first intrusion in their age, and are suited as test materials for observing the evolution of the Caledonian granitic "magma".

These are homogeneous medium-grained red or pink rocks with massive structures, without any trace of gneissic appearance and without any structural orientations. In contrast with the granites of the First Intrusion, the dark minerals are scarce here and the plagioclase is acid and unzoned. Aplitic and pegmatitic dikes are extremely rare, and so are xenoliths and hybrid rocks. The Second Intrusion ruptures conspicuously the granites of the First Intrusion and crops out in the fissure zones where it often forms small injected bodies. The age of the granites of the Second Intrusion is 320 to 340 million years [4].

Before the presentation of our results on the radioactive elements in the complexes of rocks we investigated, we must determine the reliability of such measurements. The complexity of geochemical studies of this kind is due to sampling and testing of immense areas of rock in order to obtain reliable data. The prerequisite of reliability here is uniformity of the sampling grid and a sufficiently large number of the samples [7]. Sampling was done by composites, each of which consisted of 8 to 15 pieces of the rock. Some samples consisted of 30 to 60 lumps (for large areas and for sedimentary profiles

of diverse composition). Fragmentation and reduction in bulk were done by the commonly accepted procedures.

The analyses were conducted in two stages. The individual composites were analyzed first. The results were used in the calculations of the averages and in the definition of the mathematical-statistical functions characterizing the variability of the content and the reliability of the averages. Next, the combined composites were analyzed which represented all of the samples of the given complex of the rocks. The number of the analyzed samples, for every one of the four complexes, is reported in Table 1.

Table 1

Complex	Individual samples		Composites	
	No. of samples	No. of lumps*	No. of samples	No. of lumps*
M	52	800	83	1400
γ_2^2	41	500	79	900
γ_2^3	48	550	58	700
K_Z	39	1000	74	1650

*Round numbers

Table 2 shows the coefficients of variability in the content of uranium, thorium, and potassium and the coefficients of reliability of their determinations in rock complexes of different kinds, calculated on the basis of the composite samples, where v is the coefficient of variability, Sigma—the mean square deviation, m —the error of measurement of the average content, and p —the same error expressed as a percentage. The probability of m and p times 1 is 68%; the probability of 1.5 times m and p is 87%; the probability of 2 times m and p is 95%.

Table 2

Complex	γ			v			m			p		
	U	Th	K	U	Th	K	U	Th	K	U	Th	K
M	2.1	0.3	0.7	45	20	46	0.3	0.1	0.1	7	3	7
γ_2^2	1.7	0.4	0.6	24	17	15	0.4	0.1	0.1	6	5	4
γ_2^3	2.8	0.8	0.6	36	27	17	0.9	0.3	0.2	11	10	5
K_Z	2.6	0.9	0.9	37	43	29	0.5	0.2	0.2	7	9	6

We understand clearly the fact that the methods of mathematical statistics may be applied only tentatively, in our case, and yet they do represent a certain objective criterion of reliability of the averages, as well as of the variations in the concentrations of the elements in different parts of the area.

Table 3 presents the results on uranium, thorium, and potassium in the complexes of rocks here investigated. Columns "1" show the averages of all the analyses; Columns "2"—the analysis of the combined sample of all composites; Columns "3" ("Ave.") is the average of "1" and "2". The agreement between analysis of the composites and the average of the individual analyses is entirely satisfactory.

Table 3

Complex	U, N x 10 ⁻⁴ %			Th, n x 10 ⁻³ %			K, n %		
	1	2	Ave.	1	2	Ave.	1	2	Ave.
M	3.4	2.9	3.2	0.9	1.0	1.0	1.6	1.8	1.7
γ_2^2	3.7	4.0	3.9	1.6	1.7	1.7	3.6	3.3	3.4
γ_2^3	5.6	6.4	6.0	2.5	2.7	2.6	3.7	4.2	4.0
K _Z	6.4	5.2	5.8	2.1	1.6	1.9	3.0	2.7	2.8

Uranium and thorium were determined radio-chemically [6]. Potassium was determined by Z. Ya. Kolker, by the dipycrylamine method [5]. Analysis of the combined composites was replicated four times, by two different analysts (A. M. Mavricheva and O. P. Korn).

Table 4 is intended as characteristic of the general chemical composition of the complexes. Analyses of the rocks given in this table were performed at the Chemical Laboratories of the All-Union Research Institute of Geology (Vsesoyuznyi Nauchno-Issledovatel'skii' Geologicheskii Institut) and of the Kirgizian Geologic Administration (Geolupravlenie).

In the case of the rocks of the metamorphic complex (M) and for the Cenozoic rocks (Kz), the average composite samples were analyzed. These composites were used also as controls in the determination of radioactive elements.

For the γ_2^2 granites, we took the average of eight analyses of typical composite samples of granites and granitoids. For the γ_2^3 granites we took the average of 12 analyses of the composites of these granites.

Our averages for uranium and thorium in the Terskei Ala-Tau Caledonian granites are somewhat lower than the earlier results obtained by L. V. Komlev [2] which were accepted by Tauson and others for the Tyan-Shan Batholith (Susamyr) [8]. We may now draw certain conclusions from the data reported in the tables.

Table 4. Chemical Composition of Principle Complexes of Rocks in Terskei Ala-Tau Mountains (per cent by weight)

Constituents	Complexes			
	M	γ_2^2	γ_2^3	K _Z
SiO ₂	51.28	67.25	74.49	60.59
TiO ₂	0.60	0.40	0.12	0.54
Al ₂ O ₃	12.40	14.95	12.59	13.85
Fe ₂ O ₃	1.68	1.53	1.54	3.72
FeO	4.40	3.50	0.82	1.68
MnO	0.10	0.06	0.05	0.09
MgO	5.26	0.93	0.21	1.75
CaO	10.08	2.47	0.91	5.80
K ₂ O	2.22	4.00	5.11	3.35
Na ₂ O	1.98	3.17	3.45	2.18
H ₂ O	0.34	0.38	0.12	0.72
Loss on ignition	9.60	1.16	0.77	5.95
Sum	99.94	99.80	100.18	100.22

1. Appreciable quantities of radioactive elements—uranium, thorium, potassium—were introduced with the granitic intrusions.

2. Granites of the Second Caledonian Intrusion (alaskites) contain appreciably more radioactive elements than granites of the First (the Main) Intrusion (porphyry-type granites and granodiorites).

3. The variation coefficients for the content of radioactive elements here determined (v) are commensurable for all of the complexes and for all of the elements, although we may note here certain relationships, namely:

a) The v is generally higher for sedimentary rocks (except for Th, the "M" Suite).

b) In granites of the Second Phase, the v for Th and U is noticeably higher than in granites of the First Phase. This may be explained by differences in the size, the structural types, and the expressions of post-magmatic processes in individual granitic bodies of the Second Phase.

4. On comparison of total chemical analyses of the host rocks (M'') and of the granites of the Main (the First) Intrusion (y), whose development may be regarded as the result of some kind of a granitization, we may observe significant differences in their chemical characteristics.

Formation of a granitic intrusion (as by replacement of host rocks) accompanied by a substantial introduction of silicon, alkalies, and, to a small extent, of aluminum (together with the radioactive elements). Concurrently, there is an appreciable outward migration of calcium and magnesium, and, to a lesser degree, of iron, manganese, and uranium. This tendency is progressive (excepting aluminum) in the

granites of the Second Phase (γ_2) which are the result of further developments of the Caledonian intrusive activity.

5. Chemical composition of Cenozoic sediments (K_z) and their radioactivity are about the average between the rocks of the metamorphic series and the granites. Granitic intrusions, in this case, have a definite effect on the content of the majority of the elements. A more detailed analysis of this proposition would not be feasible, in the instance of this relatively limited section of the earth's crust.

We should merely remark that the appreciable increase in the amounts of U (and, to some extent, of Th) in Cenozoic sediments cannot be explained entirely as the result of admixture of the porphyry-type granites (γ_2). We should remember, in this connection, the fact that the Cenozoic sediments are composed chiefly of materials derived from degradation of the roof of the batholith, which are significantly high in radioactive elements (especially uranium), and of a small amount of materials from the more active young intrusions.

6. Preliminary data suggest that the relationships and the general orders of magnitude of the concentrations of the elements here studied appear to be sustained throughout a much *larger* territory of the Tyan-Shan.

The work was done at the laboratory of I. E. Starik, whose valuable advice and aid are deeply appreciated by the author.

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RADIOACTIVE ELEMENTS IN IGNEOUS ROCKS OF
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Abstract

Radioactive element contents have been determined for intrusive and effusive rocks of North Kazakhstan. The possibility has been shown of using radioactivity as additional indicators in defining intrusive complexes of North Kazakhstan and similar regions. The variations of the content of radioactive elements in igneous rocks are related to the different composition of intrusive and effusive bodies as well as the process of uranium migration and, to a lesser extent, to thorium migration in the course of magmatic activity. The different migration ability of these elements is related to the presence of easily soluble, as well as to sparingly soluble uranium in the rocks.

A large body of data on radioactivity of rocks from different parts of the earth has been now assembled. However, most of the studies deal with radioactive elements in granitoids of individual intrusive bodies [9] or, at most, in individual intrusive complexes [6, 7, 10, 11].

A major problem in metallogenic investigations is the determination of radioactive elements in sedimentary and magmatic rocks, in the sequence of their formation, concurrent with the formation of the mobile zones. As a rule in cases of this kind we have to deal with magmatic rocks of several intrusive complexes developing regularly during the early, the intermediate, and the late stages of the process, according to Ya. A. Bilibin [2].

The present study is concerned with the radioactive elements in igneous rocks of the part of Northern Kazakhstan where an intensive accumulation of sediments, magmatism, and formation of folded structures were taking place during Lower Paleozoic time. The article reports the results of direct determinations of uranium by the luminescent method involving chemical decomposition of the samples by a mixture of hydrochloric and sulfuric acids and ammonium fluoride (± 10 to 20% error of the analysis) and of the determinations of thorium radiochemically (± 5 to 10% error of the analysis) in samples collected during 1954 - 1957 by the author and by other co-workers of the A. I. Semenov team: V. S. Malyavkin, N. N. Marochkin, and Yu. M. Shuvalov.

Determinations of the easily soluble uranium* were done by the luminescent method involving the decomposition of samples by dilute sulfuric acid at 30 to 40°C, under conditions in which tetravalent uranium is only slightly dissolved or oxidized [1]. Consequently, we may

*In Tables 1 through 4 and in Figures 2,3 and 4, the U_{ss}/U_{es} ratio is the ratio of sparingly soluble to easily soluble uranium.

believe, on the first approximation, that concentrations of the easily soluble and of the sparingly soluble uranium may be representative of the hexavalent and of the tetravalent uranium respectively, to a certain degree.

Samples consisting of several pieces of the rock, with a total weight of 0.5 to 1 kilogram, were collected from an area 1 meter square, on the basis of the simultaneous measurement of the gamma radiation by which the radiation of the rock volume of about the same surface area was determined [8].

The Lower Paleozoic geosynclinal zone and the folded belt which was formed, with this zone as the base, had undergone a prolonged and complex evolution, in the territory of the Northern Kazakhstan, terminating in a complete drainage of this territory and in its passage into a stable platform state. This entire period is divided into several stages, by A. I. Semenov:

The initial and the early stages—developments of the (PCm-Cm) geosyncline; the intermediate stages—further development of the geosyncline and its conversion into a folded belt (O-S?); the late and the terminal stages—development of the folded belt and its conversion into a platform (D₁₋₂-D₃). The characteristic volcanism and intrusive activity were associated with every one of these stages. Flows of basic and intermediate lavas, with the uranium and thorium content not over $5 \times 10^{-4}\%$ and $0.8 \times 10^{-3}\%$ respectively, were taking place in different regions of Northern Kazakhstan during the initial and the early tectonic stages. Dikes and small stocks of gabbro and diabasic gabbro, some of which functioned as conduit channels for the effusives, contain less uranium than is present in the effusives. On the whole, this type of rock contains the same concentrations of uranium and thorium, as a rule, that are characteristic of the basaltic layer of the earth's crust [5], except in places where they come close to the highly radioactive Precambrian rocks, where basic effusives with a somewhat higher content of radioactive elements may be found.

Massifs of the batholithic type were formed during the intermediate stages. Three complexes are recognized among these bodies of rock: the Krykkuduk, the Zerendinsk, and the Borovskoe. Locally, there are also some flows of basic and intermediate effusives containing small amounts of uranium, generally 1 to $1.5 \times 10^{-4}\%$. The uranium may be as high as 2 to $3 \times 10^{-4}\%$ in some particularly acid effusives.

Biotite-hornblende diorites, tonalites, granodiorites and granites of the Krykkuduk intrusive complex are distinguished by their low concentrations of radioactive elements. Outcrops of these rocks are situated amidst Cambrian effusive-sedimentary formations of different composition but are of monotonously uniform radioactivity. Very little of the massifs has been cut by erosion. Granites, the intrusives of this complex, in the strict sense [5] contain somewhat less uranium than the average, whereas their thorium content is not far from the average (Table 2).

Table 1

Source of sample and kind of rock	Number of analysis	Luminescent analysis		
		$U \cdot 10^{-4}\%$	Number of analysis [†]	$\frac{U_{ss}}{U_{es}}$
(1) Gabbro; Zlatogorsk Massif; W part of Northern Kazakhstan.	3	0.4	3	100
(2) Diabases and diabase porphyrites; W part of Northern Kazakhstan	17	1.1 ± 0.3	2	300
(3) Diorite porphyrites; central part of Northern Kazakhstan	4	1.5	-	-
(4) Diabases and diabase porphyrites; E part of Northern Kazakhstan	18	0.9 ± 0.2	-	-
(5) Gabbro; small bodies; E part of Northern Kazakhstan	2	0.6	-	-
(6) Formations in the basaltic layer of the earth's crust	-	0.9	-	-

	Number of analyses	Radiochemical analysis			
		$Ra \cdot 10^{-10}\%$	$U_{eq}^* \cdot 10^{-4}\%$	$Th \cdot 10^{-3}\%$	Th/U^{\dagger}
(1)	-	-	-	-	-
(2)	1	0.4	1.2	0.3	3.0
(3)	1	0.8	2.4	0.8	4.0
(4)	-	-	-	-	-
(5)	-	-	-	-	-
(6)	-	0.3	0.9	0.4	-

* U_{eq} is the uranium calculated from the radium, assuming their equilibrium.

† Presumably for comparisons between the sparingly and the easily soluble uranium. VPS

‡ It is not clear how this ratio is calculated. VPS

The low uranium in the rocks of the Krykkuduk Massif, together with their high thorium-uranium ratio, is related not only to the assimilation of the weakly radioactive host rocks but also apparently to a certain redistribution of uranium. Indeed, Figure 1 shows that the hybrid rocks that were formed at the contact zone contain less uranium than the host rocks or than granodiorites and granites in the core of the massif, whose composition is closest to that of the primary magma.

Massifs of the Zerendinsk intrusive complex are structurally the most complicated. They show sufficiently clearly the two-phase character of the magmatic intrusion. In order to investigate the distribution of radioactive elements in the rocks of this complex magmatic hearth, we tested the granitoids of the first and of the second intrusive phases (at least three radiochemical and ten luminescent analyses of every variety of the rock), as well as the dikes (1 or 2 determinations

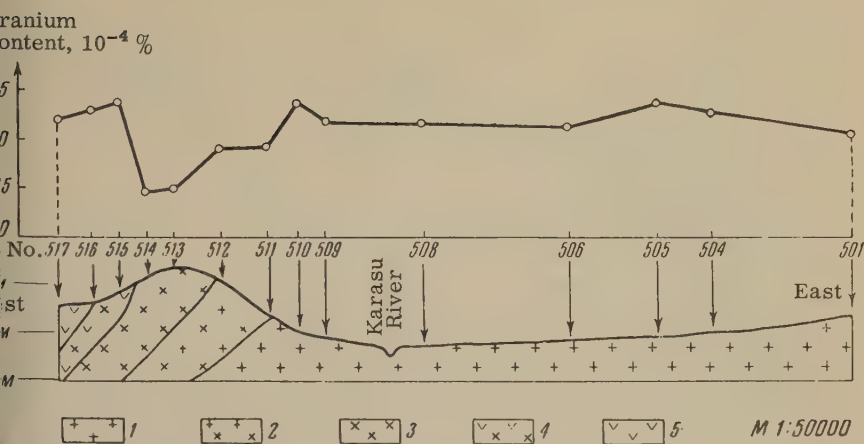


Fig. 1. Uranium in tonalites from Krykkuduk massif and from the host rocks. Samples collected on traverse across the massif: 1—Biotite-hornblende quartz porphyrites; 2—hybridized diorites; 3—hybrid rocks; 4—hornfelsized porphyrites and their tuffs; 5—porphyrites and Ordovician tuffs.

radium, uranium, and thorium). The results are shown in Figure 2, diagrams of the concentrations of radioactive elements and of their relationship in the rocks, as influenced by the time of formation of the granitoids. This figure indicates that the lowest concentrations of uranium and thorium are fixed in granosyenites, granodiorites, and biotitic porphyroid granites of the First Intrusive Phase which had developed in contact with Cambrian and Precambrian rocks.* A high thorium-uranium ratio and a preponderance of sparingly soluble uranium are characteristic of these granitoids. As depth of the erosion surface increases, there is an increase in the concentrations of uranium in biotite granites, due chiefly to accessions of the easily soluble uranium and, to a lesser extent, of thorium, which leads to a gradual lowering of the thorium-uranium ratio. And, finally, in masses with a deep erosion surface, the biotite granites and leucocratic granites, which are generally in the central parts of the plutonic bodies, contain up to 10 to $12 \times 10^{-4} \%$ uranium.

Still higher concentrations of radioactive elements, but about the same thorium-uranium ratio (3 or 4), are observed in granitoids of the Second Intrusive Phase and in the acid dikes. There is again an increase in the Th/U ratio and in the sparingly soluble uranium in the youngest vein formations of the Zerendinsk intrusive complex (diabasic gabbro and diorites).

It is evident, therefore, that there was a certain increase of uranium and, to some extent, of thorium, in the rocks that were crystallized in

these Cambrian and Precambrian rocks contain $1 \times 10^{-4} \%$ to $10 \times 10^{-4} \%$ uranium, with the average of $3 \times 10^{-4} \%$ [4].

Table 2

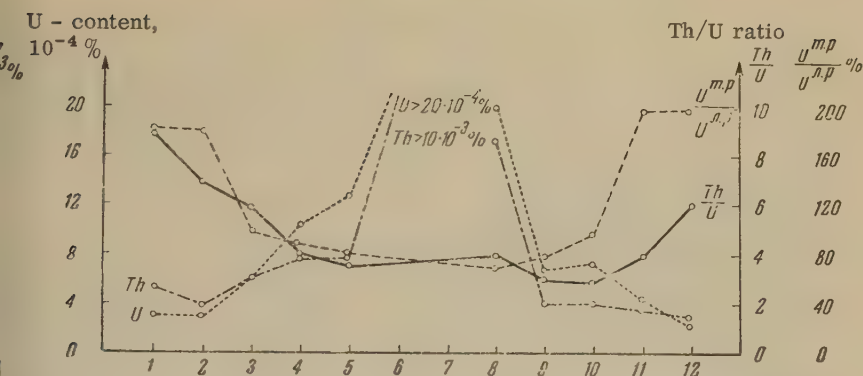
Source of sample and kind of rock	Number of analyses	Luminescent analysis		
		$U \cdot 10^{-4}\%$	Number of analyses*	U_{ss}/U_{es}
(1) Host rocks: Porphyrites, their tuffs, sandstones, etc.	>40	$1.5 \pm 0.5^\dagger$	-	-
(2) Hybrid rocks of gabbroid composition	5	0.5	-	-
(3) Biotite-hornfels quartz diorites	46	1.2 ± 0.4	7	50 to 200
(4) Granodiorites and granites	22	1.8 ± 0.5	4	50 to 200
(5) Acid dikes	21	2.6 ± 1.0	4	150
(6) Microdiorite dikes	5	1.8	1	180
(7) Porphyrite dikes	12	1.0 ± 0.2	3	200

	Number of analyses	Radiochemical analysis			
		$Ra \cdot 10^{-10}\%$	$U_{eq} \cdot 10^{-4}\%$	$Th \cdot 10^{-3}\%$	Th/U^{**}
(1)	-	-	-	-	-
(2)	-	-	-	-	-
(3)	3	0.5	1.5	0.8	8.0
(4)	4	0.6	1.8	1.4	7.0
(5)	3	1.0	3.0	1.1	3.7
(6)	1	0.7	2.1	0.7	4.0
(7)	3	0.5	1.5	0.6	5.0

*We have in mind the variations in the U-content of the rocks.
† Probably the number of comparisons between the sparingly and the easily soluble uranium. VPS
‡ Probably U calculated from Ra, assuming equilibrium.
** It is not clear how this ratio was calculated. VPS

the deeper horizons, during cooling of this complex magmatic hearth so highly enriched in radioactive elements. This phenomenon should be related apparently to migrations of the mobile uranium compounds both in tonalites and in granodiorites of the Krykkuduk intrusive complex. The Th/U ratio differences in the Zerendinsk granitoids (Fig. 2) and the fluctuations in proportions of the easily and the sparingly soluble uranium are probably indications of different paths of migration of uranium and thorium, especially during the early and the terminal stages of the cooling of the massifs. The presence of easily soluble uranium (up to 40 to 50% of the total) was noted in samples of biotite granites taken from boreholes at 150 to 200 meters depths.

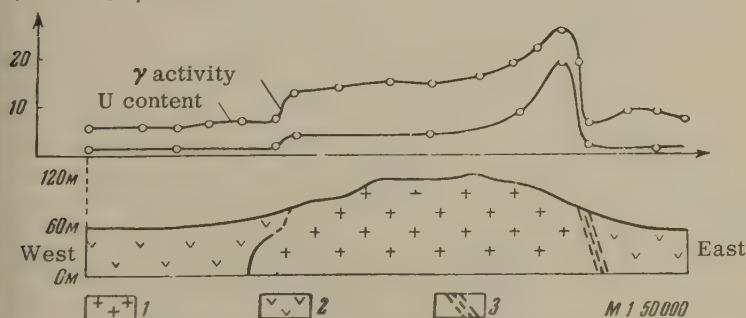
Granitoids of the Borovskoe intrusive complex (Fig. 3) differ but insignificantly from the Zerendinsk granites in their uranium content. At the same time, intrusive bodies of the Borovskoe complex are conspicuously high in gamma radiation and in concentrations of uranium and thorium, against the background of country rocks and in comparison



2. Amounts and relationships of radioactive elements in granitoids of the Zeredinsk Intrusive Complex, in relation to the time of the crystallization of the rocks: I—Intrusive Phase: 1—syenites, granosyenites, granodiorites; 2—biotitic porphyry-like granites in the upper parts of the intrusive bodies; 3—biotitic porphyry-like granites in the central parts of the intrusive bodies; 4—biotitic and leucocratic granites in the central parts of the intrusive bodies. II—Intrusive Phase: 5—fine-grained leucocratic granites and granite-porphyrtes; 6—albitic granite-porphyrtes and greisenized granites. The dike facies: 7—granite-porphyrtes; 8—pegmatites; 9—felsites; 10—aplites; 11—granodiorites and diorites; 12—gabbro-diorites.

h other massifs belonging to the intermediate stages. The thorium-uranium ratio is low in the Borovskoe granitoids, which is also characteristic of the Zeredinsk granites with a deep erosion surface. Increases in gamma radiation and uranium content were established in the marginal part of one of the Borovskoe massifs (the Karabulak) (Fig. 3). The increase in uranium in the endocontact of this massif is related probably to migrations of mobile uranium compounds into the low pressure zone which developed in coincidence with the zone of fractures during cooling

U content, 10^{-4} %, and
 γ activity, μ r g per hour



3. Gamma-activity and uranium content of granites from Karabulak Massif of the Borovskoe Intrusion Complex and of traverse across the Massif: 1—granite-porphyrtes and their tuffs; 2—porphyrites and their tuffs; 3—the weakened zone of fissure disturbances.

Table 3

Rock	Number of analyses	Luminescent analysis			
		$U \cdot 10^{-4} \%$	Number of analyses*	U_{ss}/U_{es}	
(1) Host rocks: Porphyrites; porphyrite tuffs, sandstones	23	1.3 ± 0.4	-	-	
BOROVSKOE INTRUSIVE COMPLEX					
(2) Biotite-hornfels granodiorites	2	2.3	-	-	
(3) Biotitic porphyry-like granites	6	$4.5 \pm$	1	100	
(4) Leucocratic granites	4	10.0	3	50	
(5) Dikes of granites and granite-porphyrtes	1	13.0	1	50	
(6) Aplite dikes	1	4.8	1	70	
	Number of analyses	Radiochemical analysis			
		$Ra \cdot 10^{-10} \%$	$U_{eq} \cdot 10^{-4} \%$	$Th \cdot 10^{-3} \%$	Th/U
(1)	-	-	-	-	-
BOROVSKOE INTRUSIVE COMPLEX					
(2)	-	-	-	-	-
(3)	3	1.7	5.1	1.6	3.5
(4)	1	3.4	10.2	3.6	3.6
(5)	-	-	-	-	-
(6)	-	-	-	-	-

* Probably the number used in the calculation of the U_{ss}/U_{es} ratio. VPS

† Probably calculated from Ra, assuming radium-uranium equilibrium. VPS

‡ It is not clear how this ratio is calculated. VPS

of the magma. This phenomenon was established by Gross [13] and by other investigators in small granitoid stocks.

Flows of acid lavas and, more rarely, of alkali and basic lavas and formation of small intrusive bodies and dikes were taking place during the late stages of the formation of the folded belt. The expressions of magmatism were controlled by deep fracture zones. Several complexes are recognizable among the intrusive rocks of the late stages (the Stepnyak complex of small intrusions; the Ishim alkali complex; the complex of sub-volcanic intrusions; the complex of leucocratic granitoids; the dike complex). Intermediate and basic rocks of the Stepnyak complex (0.5 to $1.2 \times 10^{-4} \%$ U; 0.4 to $0.6 \times 10^{-3} \%$ Th) do not differ appreciably in their content of the radioactive elements from the formations of the Krykkuduk massif. Figure 4 does not take into account in its diagrams the concentrations of uranium and thorium in the rocks of the Stepnyak because the problem of the differentiation of the complex is not yet definitely solved. Epileucitic* and trachyte porphyries are the most radioactive rocks of the late stages ($U = 7 \times 10^{-4} \%$;

*Fine-grained porphyry-like rock in which leucite is replaced by orthoclase. V

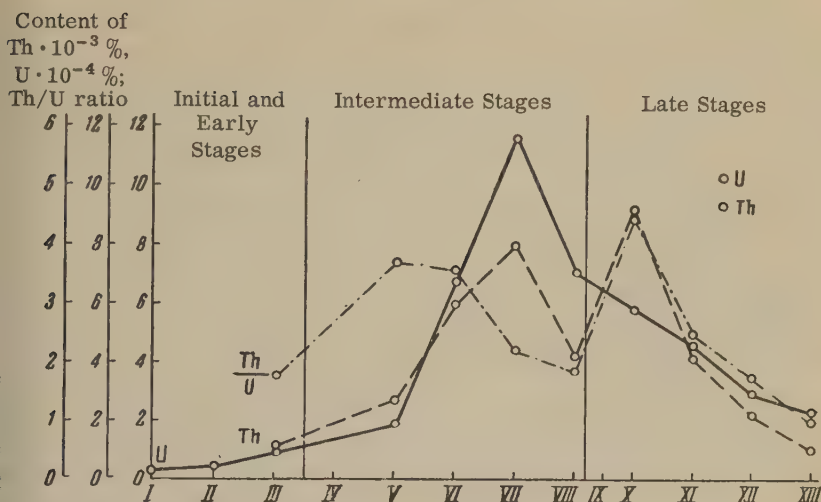


Fig. 4. Diagram of stage distribution of uranium and thorium in igneous rocks of Northern Kazakhstan: I—Gabbros and amphibolites of the Chalkar massif; II—gabbros and gabbro-norites of the Zlatogorsk massif; III—diorites and diabase porphyrite Cm; IV—Ordovician diorite porphyrites; V—granodiorites and granites of the Krykkuduk intrusive complex; VI—granitoids of the First Intrusive Phase, the Zerendinsk complex; VII—granitoids of the Second Phase, the Zerendinsk complex; VIII—granitoids of the Borovskoe intrusive complex; IX—diorites and granodiorites of the Stepnyak complex; X—alkali rocks of the Ishim complex; XI—Acid effusives D_{1-2} ; XII—The complex of leucocratic granitoids; XIII—The dike complex.

$= 4 \times 10^{-3} \%$), together with muscovitized and nepheline syenites $= 6 \times 10^{-4} \%$; $\text{Th} = 4.6 \times 10^{-3} \%$) and the dikes of the Ishim alkali complex.

The Devonian acid effusives in different regions of Northern Kazakhstan contain uranium in quantities approaching the average, and somewhat higher than the average quantities of thorium (Table 4). Sparingly soluble uranium is preponderant in the samples. The rocks of quartz porphyries (granite porphyries, plagioclase-granite porphyries) functioning as conduit channels for acid effusives are less radioactive, and the prominence of the sparingly soluble uranium is more conspicuous in these rocks.

Granitoids belonging to the complex of minor intrusives and whose aluminosity and basicity are above average in contrast with the granite-porphyrates, contain somewhat less uranium and thorium, characteristically; their thorium-uranium ratio is relatively low, and their content of easily soluble uranium is high.

Dikes of diorite and diabase porphyry and of sodium syenites are the largest intrusives in the Northern Kazakhstan territory. They are located in tectonically disturbed zones and they control the endogenic mineralization. In contrast with the basic dikes belonging to the early

Table 4

Rocks	Number of analyses	Luminescent analysis		
		$U \cdot 10^{-4}\%$	Number of analyses*	U_{ss}/U_{es}
(1) Acid effusives, D ₁₋₂	27	4.5 ± 1.5	7	150
(2) Granite porphyries, the sub-volcanic intrusive complex	19	3.2 ± 1.0	3	200
(3) Alaskite granites, grano-syenites, syenite-diorites; the leucocratic granitoid complex	51	3.0 ± 1.2	5	70
THE DIKE COMPLEX				
(4) Sodium syenites, E part of Northern Kazakhstan	10	3.1 ± 1.5	3	90
(5) Diorite porphyrites, same place	7	1.8 ± 0.5	6	100
(6) Diorite porphyrites	8	2.2	2	100
(7) Ditto	5	16.0	-	-

	Number of analyses	Radiochemical analysis			
		$Ra \cdot 10^{-10}\%$	$U_{eq} \cdot 10^{-4}\%$	$Th \cdot 10^{-3}\%$	Th/U
(1)	5	1.6	4.8	2.3	5.0
(2)	3	1.1	3.3	1.6	5.5
(3)	8	1.0	3.0	1.1	3.5
THE DIKE COMPLEX					
(4)	5	1.0	3.0	0.5	1.7
(5)	4	0.7	2.1	0.5	2.5
(6)	2	0.6	1.8	0.4	2.0
(7)	2	4.5	13.5	1.3	1.0

*) Probably the number used in the $U_{ss} - U_{es}$ comparisons. VPS

† Calculated from Ra , on the assumption of the $Ra - U$ equilibrium. VPS

‡ Probably the ratio of dtd. Th to U_{eq} . VPS

and the intermediate stages of the evolution, the biotite-hornblende diorite and diabase porphyries of the late stages contain small amount of thorium and relatively high amounts of uranium (Table 4), with a noticeable prominence of the easily soluble uranium. The low thorium uranium ratio is noted in the young dikes of all types, which is not characteristic of the other rocks of Northern Kazakhstan.

CONCLUSIONS

1. In the magmatic process, there is a gradual increase in radioactive elements and in the thorium-uranium ratio in the younger igneous rocks, up to the end of the Intermediate Stages (Fig. 4). Further on, in the Late Stages, there is a decrease in the radioactive elements and in the thorium-uranium ratio. In many respects, a similar distribution of radioactive elements in igneous rocks was established,

some investigators, for some other folded regions of the USSR (Eastern Tuva, Kandyktas Mountains, etc.). Such distribution is apparently characteristic of metallogenically similar mobile zones of the Earth's crust. Comparisons of the behavior of the radioactive elements in magmatic processes in folded areas of different kinds should be highly important.

2. Igneous rocks belonging to different intrusive complexes of Northern Kazakhstan differ significantly from each other in their content of the radioactive elements, as a rule. In the studies of metallogenesis in such zones the data on radioactivity of rocks may render substantial aid in the identifications of intrusive complexes and in their classification as belonging to some definite stage of geosynclinal developments or of zones of folding.

3. The phenomenon of enrichment of the radioactive elements in the cores of intrusive bodies was noted only in one massif, in Northern Kazakhstan, which was formed apparently in the environment of intense tectonic activity. According to the available data, there is rather impoverishment of the tops of plutonic bodies, with respect to uranium, in the case of intrusions of the batholithic type. The observed proportions of uranium and thorium cannot be explained entirely by an assimilation of the radioactively weak host rocks, though this process may play an important role in the distribution of the radioactive elements.

The absence of uranium halos in host rocks, as well as the enrichment of radioactive elements in the central parts of the massifs, indicates probably a certain downward migration of uranium and possibly also of thorium during cooling of the plutonic body. Later on there is migration of radioactive elements into the upper horizons, concurrent with the entry of granitoids of the Second Intrusive Phase and of dikes. There is a kind of "cycle" of uranium during the development of the magmatic hearths, in the Intermediate Stages.

4. The invariable presence of the easily soluble uranium was demonstrated both in surficial samples and in samples from the 100 to 200 meters depths, in the igneous rocks of different composition and age, in Northern Kazakhstan. It is highly probable that hexavalent uranium is present, along with tetravalent uranium, already at the time of the formation of magmatic rocks. The presence of easily soluble uranium is recorded by L. V. Tauson [9], S. Y. Tomkeieff [12], and by other investigations [10, 13]. Apparently its presence is decisive in the migration of uranium and in the formation of rocks with different thorium-uranium ratios.

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THE STATISTICAL METHOD OF DETERMINING THE HOMOGENIZATION TEMPERATURE OF LIQUID INCLUSIONS

Measurements of the Temperature of
Crystallization of Quartz from Solutions

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Abstract

The authors apply the law of large numbers to the interpretation of the data obtained from numerous determinations of apparent temperature; they have utilized the method of homogenization of liquid-gas phases of the inclusions from quartz crystals of various occurrences. The histograms and the frequency curves represented give the possibility to appreciate the frequency maxima and variation limits of the crystallization temperature in the same quartz crystal at different points of the same deposit; they permit also some conclusions about the geothermal gradient of the ascending hydrothermal solutions.

Among the many methods on record of determining the temperatures at which rocks and minerals are formed, there is the method of the homogenization of the gas-liquid phases that may be present, as inclusions, as in quartz. This method, here to be described, has been studied in its greatest detail by numerous authors, including many famous Soviet scientists. Thus G. G. Lemlein [1] cites more than one hundred papers devoted to this method.

There have been critical investigations with the purpose of testing the suitability of this method. E. I. Vulchin [2], in his studies of various heterogeneous systems resembling, in their composition, liquid inclusions in minerals, concluded that the homogenization method is applied only to systems whose pressures and temperatures are not particularly high. We may accept the critical temperature of water as the upper limit.

The authors of the present article had measured the temperatures at different parts of transparent quartz crystals of different origin [3, 4].

The sample is heated gradually in a paraffin oil bath. The oil is heated electrically, so as to raise its temperature up to 70°C, and at a rate of 0.5°C per minute near the homogenization temperature. It was possible to observe experimentally that the homogenization temperature varies within a definite range for one and the same

crystal. For example, a crystal of quartz from Nikulitel (Northern Dobrudzha, Rumania) had a range from 94 to 115°C; another crystal, from 103 to 126°C, etc. These facts indicate that there are differences in the degree to which the cavities in the quartz crystal are filled and consequently, that the cavities were formed in a changing environment. Some of the variations in the environment were accidental, whereas some of its other aspects were essentially constant.

In order to eliminate the accidental factors, we applied the principle of large numbers, in relation to the fairly large number of our measurements of the homogenization temperatures.

Table 1 reports the homogenization temperatures for inclusions in crystals of secondary quartz taken from several fissures in quartz sandstone in the open cut of the Dervent Malkochi Hill, Northern Dobrudzha. The sandstone is believed to be Verfenian.*

The results in Table 1 show that there are appreciable differences in the individual measurements of the homogenization temperature. It follows, therefore, that there is no consistency in these measurements and the method** is not suited for the purpose.

If, however, the homogenization temperatures are treated statistically, the resulting histogram becomes a curve, quite regular in the frequency distribution and also symmetrical in its two arms (Fig. 1). One may assume, under the circumstances, that the arms of this curve represent concrete examples of the predominance of accidental factors during crystallization, whereas the maximum frequencies represent ordinary conditions. The arithmetical mean for the homogenization temperature of the inclusions in the Malkochi crystals is: $M_{104} = 136.8^{\circ}\text{C}$; it corresponds to the temperatures characteristic of the maximum frequency of the results.

We should mention also that Grushkin [6] constructed analogous diagrams for fluorspar, on the basis of numerous determinations of the homogenization temperature. He points out that individual measurements of the temperature give only relative results in appraisals of the depth at which the given deposit was formed.

The second example chosen by us is the quartz veins cutting through diabase rocks of subaqueous origin (Nikulitel, Northern Dobrudzha). This diabase is Middle Triassic in age.

We examined crystals from the following veins at the Nikulitel: a) The Main Vein, Tugulea Hill; b) The Eastern Group; c) Vein 1, Dealul din Miilek Hill; and d) Vein 2, Dealul din Miilek Hill.

The diagram for the main vein of the Tugulea Hill shows that the homogenization temperatures range from 90 to 130°C (Fig. 2). The temperature curve is asymmetric, with the highest frequency between 110 and 120°C, and with the arithmetical average somewhat less than

*"Verfenian" is synonymous with "Scythian" which is the lowermost division of the Triassic. VPS

**I. e., that any single measurement of the homogenization temperature means very little by itself. VPS

Table 1. Derwent Stone Open Cut Quarry - Mal'Kochi

m n.	Crystal no.	Diam. of gaseous bubble mm	Homogeni- zation temp. °C	Item no.	Crystal no.	Diam. of gaseous bubble mm	Homogeni- zation temp. °C
	11	0.01	128	53	5	0.01	135
	11	0.02	133	54	5	0.02	130
	11	0.01	128	55	6	0.01	130
	11	0.02	135	56	6	0.02	147
	11	0.02	140	57	6	0.01	135
	12	0.02	143	58	6	0.01	149
	12	0.01	138	59	6	0.02	140
	12	0.02	141	60	6	0.01	152
	12	0.01	132	61	6	0.01	145
	12	0.01	139	62	6	0.01	138
	12	0.02	140	63	6	0.01	134
	12	0.01	134	64	7	0.01	140
	13	0.01	139	65	8	0.01	136
	13	0.01	136	66	8	0.01	145
	13	0.01	133	67	8	0.01	129
	13	0.01	134	68	8	0.02	146
	13	0.02	136	69	8	0.01	140
	13	0.02	129	70	8	0.01	134
	13	0.01	143	71	8	0.01	136
	13	0.01	144	72	8	0.01	146
	1	0.02	142	73	8	0.01	137
	1	0.01	133	74	8	0.01	147
	1	0.01	130	75	8	0.02	148
	1	0.02	140	76	8	0.01	145
	1	0.01	135	77	8	0.01	143
	1	0.01	137	78	8	0.01	138
	1	0.02	145	79	8	0.01	135
	1	0.02	141	80	8	0.01	128
	1	0.01	132	81	8	0.01	137
	1	0.01	139	82	9	0.02	140
	2	0.01	135	83	9	0.01	127
	2	0.01	133	84	9	0.01	139
	2	0.01	127	85	9	0.01	143
	2	0.01	130	86	9	0.01	133
	2	0.01	142	87	9	0.01	135
	2	0.01	135	88	9	0.01	138
	2	0.01	140	89	9	0.02	145
	2	0.01	136	90	9	0.01	131
	3	0.01	134	91	9	0.01	127
	3	0.01	130	92	9	0.01	138
	3	0.02	140	93	9	0.01	135
	4	0.01	130	94	9	0.01	140
	4	0.01	127	95	9	0.01	124
	4	0.01	136	96	9	0.01	137
	4	0.01	140	97	9	0.01	136
	5	0.01	132	98	9	0.01	129
	5	0.01	127	99	9	0.02	139
	5	0.09	134	100	9	0.01	128
	5	0.01	138	101	9	0.01	124
	5	0.02	141	102	10	0.01	135
	5	0.01	145	103	10	0.02	143
	5	0.02	143	104	10	0.01	147

$M_{36} = 113^{\circ}\text{C}$. It may be easily seen that another increase in the frequency, in the vicinity of 100°C , results in a distortion of the left arm of the curve.

The diagram for the eastern group of veins, Tugulea Hill (Fig. 3) shows only one maximum at the 115 to 120°C temperature range, corresponding to the arithmetical mean of $M_{31} = 117^{\circ}\text{C}$. As in the case already cited, this latter curve also shows a second maximum between 100 and 105°C , in its left arm. There are two distinctions, however, in the second case (both accidental), with the much higher homogenization temperatures at about 154° and 167°C .

Table 2 shows the mean homogenization temperatures and the range of their variation for individual crystals. This range varies from 1° to 72°C , depending on the crystal. Table 3 shows the mean homogenization temperatures calculated separately for each of the deposits. It shows also the temperatures within the range of the maximum frequency.

One may see, in this particular case, that the temperatures are very close to the temperatures indicated for different veins of one and the same deposit, as well as for more than one deposit in one and the same hill. Thus the mean temperature for the Tugulea Hill is $M_{72} = 114.8^{\circ}\text{C}$ with the maximum frequency within the 115° to 120°C limits, whereas the mean for the Dealul din Miilek is $M_{88} = 124^{\circ}\text{C}$, with the maximum frequency between 125° and 130°C .

The frequency curves, representing percentages, are summarized in Figure 4, for the sake of comparisons between different deposits. We may conclude from this diagram that the curves show displacement of the frequency of the maxima, in the case of the Tugulea Hill and the Dealul din Miilek Hill, as well as displacements of both the lower and the upper limits of the homogenization temperatures. One may see the departures in the left branch of both curves.

The frequency curve was built on the base of the same diagram. This curve was characteristic for the 160 temperature measurements on the quartz crystals from Nikulitel. The arithmetical average

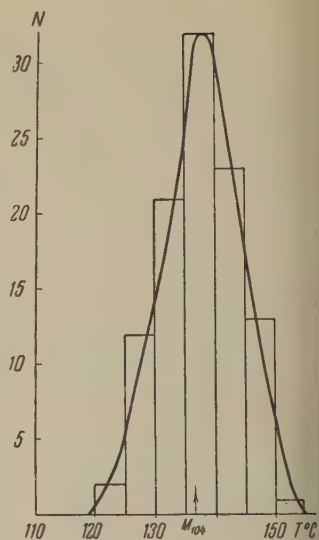


Fig. 1.

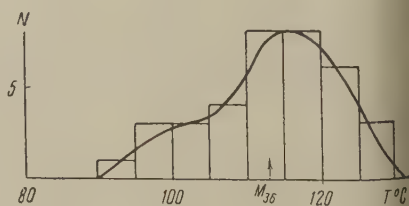


Fig. 2.

homogenization temperature is $T_0 = 119.7^\circ$ with the customary situations the temperature between 90° and 140°C .

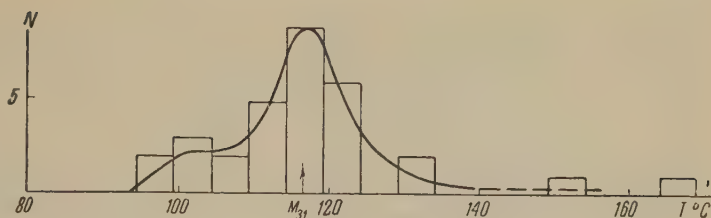


Fig. 3.

The third illustration, the most complicated one, is a hydrothermal deposit of a sulfide complex at Gerzha, near Baia Mare (Mararesh). Let us present here the characteristics of the "O" Vein of this deposit in which several levels were exposed. The levels sampled and the quartz were as follows: a) The Matei Level; relative depth 0 meters; b) The "O" Level (the Ioachim); relative depth 70 meters; c) The II Level; relative depth 130 meters.

The diagram of Figure 5 shows the frequency curves of the homogenization temperatures. The fact that the temperatures of the maximum frequency increase with depth is taken into account in this diagram. The average homogenization temperature also increases with depth.

Table 4 shows the relative homogenization temperatures for the "O" Vein.

The second vein, "Mekhtige", is represented by samples from the 325 m depth (relative to the depth of the Matei Horizon). The curve of the homogenization temperatures has two maxima: one at 145 to 250°C and another at 275 to 290°C (Fig. 6). This shape of the curve indicates two temperatures at which, in the main, the deposition of quartz crystals was taking place. These temperatures were, however, with depth, the temperatures already reported for the "O" Vein.

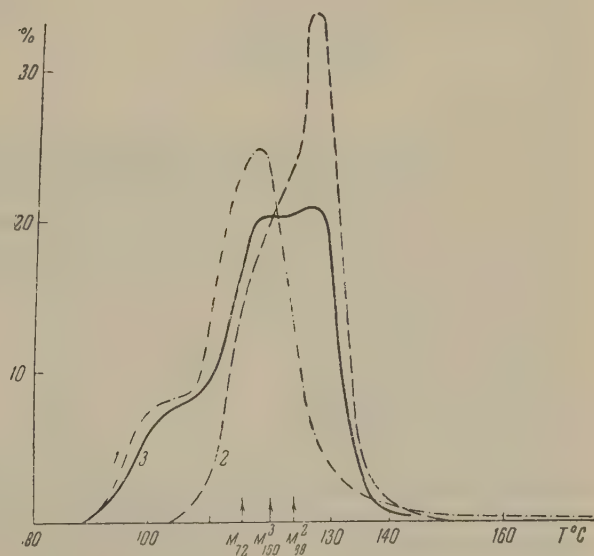


Fig. 4.

Fig. 6 shows that the crystallization was taking place at temperatures represented by the two maxima. One of these maxima vanishes in the upper part of the deposit, to the point that it is not detectable in the "O" Vein.

Certain temperatures of formation of quartz begin to disappear in another ore vein; the "Shalan" (Horizon VII) ore vein diagram also shows a maximum of the order of 235 to 240°C, whereas the second maximum generally disappears, leaving only a trend toward a higher temperature, in the vicinity of 250°C in the diagram (Fig. 7).

It follows from these examples that the maximum temperatures of homogenization have a regular distribution (relative to depth). The same is observed also for the average temperatures of homogenization. Moreover, it has been established that certain quartz formation temperatures appear only at great depths but disappear in the upper sections of the profile.

Our fourth illustration is taken from a Tertiary volcanic massif in Kaliman Mountains. In certain definite parts of this massif, in the rocks that were transformed by hydrothermal activities, there are cavities and fine fissures containing small idiomorphic crystals of quartz often associated with crystals of specular hematite.

Figure 8 is a diagram of the homogenization temperatures. In this case also, two maxima are plainly visible in the curve—indications of the two temperatures at which the bulk of the quartz crystals was formed. It has been established that there are two varieties of quartz, the high and the low temperature types.

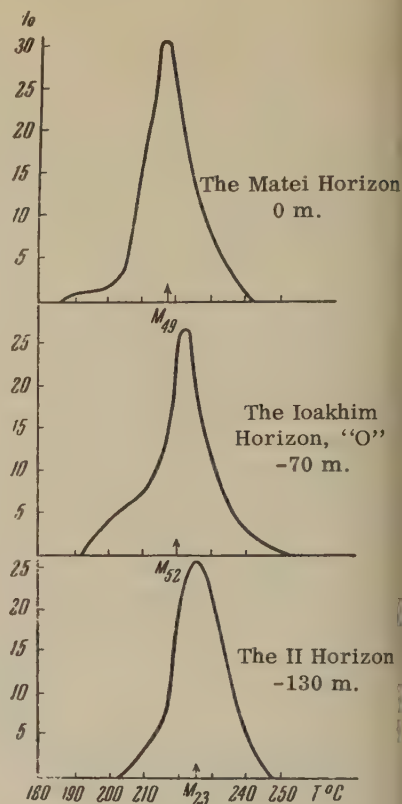


Fig. 5.

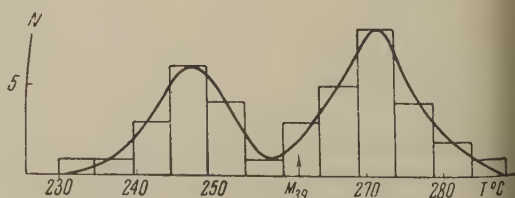


Fig. 6.

Table 2. Mean Temperatures of Homogenization and Range of Temperature Variation for Individual Crystals, Nikulitel

Deposit	Vein	Crystal no.	Mean temp., °C	Limits of variations, °C		Difference, °C
				Minimum	Maximum	
Nikulitel	"Main"	1a	116	113	118	5
	"	1b	118	110	122	12
	"	2a	117	103	126	23
	"	2b	104	94	115	21
	"Eastern group"	1	121	105	154	49
	"	2	117	95	167	72
	"	3	111	96	124	28
	"Western group"	1	112	98	129	31
	"	1a	125	113	131	18
Nikulitel din nek	"	2	121	114	136	22
	"	3	127	108	148	40
	"2"	1	127	118	133	15
	"	2	128	128	129	1
	"	3	123	120	127	7
	"	4a	129	125	133	8
	"	5	120	113	130	17
	"	6	121	113	127	14
	"	7	125	116	132	16
	Others	27	123	118	128	10

Table 3. Mean Homogenization Temperatures and the Range of Variation for Different Deposits of the Nikulitel

Deposit	Vein	Number of measurements	Mean temp. °C	Range of variation, °C			Maximum frequency °C
				Min.	Max.	Difference	
Nikulitel	"Main"	36	113	94	126	32	110 to 120
	"Eastern"	31	117	95	167	72	115 to 120
	"Western Gr"	5	112	98	129	31	-
	-	72	114.8	94	167	73	115 to 120
Nikulitel din nek	"1"	25	125	108	148	40	125 to 130
	"2"	57	124	113	133	20	125 to 130
	Others	6	123	118	128	10	-
	-	88	124.0	108	148	40	125 to 130
Average	-	160	119.7	94	167	73	-

Table 4. "O" Vein, the Gerzha Deposit

Horizon	Crystal no.	Num. of measurements	Mean temp. °C	Temperature		Limits, °C difference	Frequency, °C
				Lower	Upper		
Matei	12	10	216.9	194	232	38	-
"	13 (1)	6	221.5	213	236	23	-
"	13 (2)	33	216.9	207	230	23	-
Matei (entire)	-	49	217.4	194	236	42	215 to 220
Ioakhim	16 (2)	8	227	220	235	15	-
"	17	27	220.5	197	248	51	-
"	20	4	213.5	196	228	32	-
"	21	13	217.1	204	225	21	-
Ioakhim (entire)	-	52	220.1	196	248	52	220 to 225
II	47 (1)	21	225	208	238	30	-
	47 (2)	2	235.5	230	241	11	-
II (entire)	-	23	225.8	208	241	33	220 to 230

Crystals of both varieties were formed in neighboring cavities, within a few centimeters of each other.

CONCLUSIONS

Single determinations of homogenization temperatures may yield results representing accidental environments. For example, they may indicate higher temperatures in the upper than in the lower horizons. Application of the law of great numbers in construction of homogenization diagrams or of frequency curves yields results representing more closely the true environments of the deposition. Such results enable us to evaluate the maxima and the limits of temperature variations in one and the same crystal or to evaluate the homogenization at different depths in one and the same deposit. At the Gerzha Deposit, in the "O" ore vein, at the 130 m depth level, it has been found that the average difference in the temperature is 8.8°C, and that the corresponding apparent temperature gradient for the ascending hydrothermal solution from which the quartz has been crystallized was

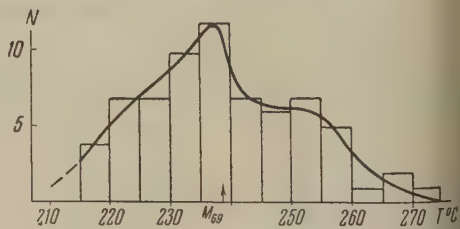


Fig. 7.

°C, per 100 m, with the corresponding geothermal gradient of 15 m · 1°C. These magnitudes proved to be analogous for the other veins of the Gerzha Deposit.

The statistical method should be applied also to solution of other problems, e.g., in ascertaining changes in the paragenesis in relation

to the homogenization temperature, in determination of zoning in some hydrothermal deposits, in determining variations in habits of minerals in relation to temperature fluctuations, in prospecting based on thermometric data, etc.

Results obtained by the statistical method, as employed in measurements of the homogenization temperature, give us an outline of the thermodynamic

environments in which the crystallization of quartz from solutions was taking place.

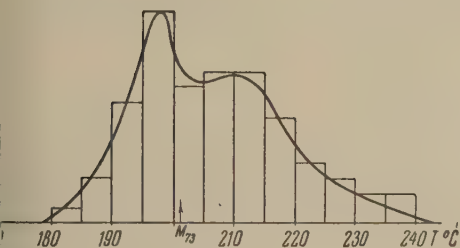


Fig. 8.

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CHEMICAL COMPOSITION OF LIQUID INCLUSIONS IN ICELAND SPAR AND GENETIC PROBLEMS

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Abstract

Relatively large liquid inclusions in perfect iceland spar crystals from various deposits of the Siberian shield connected with trap formation have been investigated. In the majority of cases the liquid inclusions have calcium-sodium-fluoride composition. The salt concentration in a number of inclusions is high. In one of the inclusions the salt concentration was found to be 230 g/l. In all the inclusions calcium predominates over sodium. pH of the solution of one of the inclusions was found to be equal to 5–5.5.

The absence of free CO_2 , considerable chloride concentration and the dominance of calcium chloride in inclusions indicate the specific conditions of the formation of the Siberian shield deposits. The conditions of iceland spar crystallization have been considered on the basis of mineral paragenesis and certain experiments.

Liquid inclusions in minerals are interesting from many points of view. Particular attention is attracted, moreover, by relatively large liquid inclusions, because they are suited for detailed studies of their chemical composition. Such large inclusions are rare, as a rule. They are also found in Iceland spar.

Specimens of optical calcite containing fairly large liquid inclusions were found by E. Ya. Kievenko and N. I. Andrusenko, in the course of their studies at the deposits of Iceland spar on the Siberian Platform. They passed these specimens on to the Laboratory of Magmatogenic Processes for further studies.

Vacuoles of different states of perfection (Fig. 3) were contained in the large individual crystals of Iceland spar from deposits of four different types associated with rocks of the Tunguska Complex [1]:

1. *Gonchak and Nidym Deposits.* Iceland spar associated with rhyolite lavas abounding in hydrothermal minerals.
 2. *Spar Deposit.* Iceland spar is associated with fissures in the mineralized parts of the mandelstein.
 3. *Yangurakta and Kuktule Deposits.* Iceland spar is found in mineralized zones in the tuffs.
 4. *Dzhekinde and Markhaya Deposits.* Iceland spar is associated with the mineralized parts of the crosscutting intrusions of trap rocks.
- Chemical composition of liquid inclusions was determined by two procedures. The first one consisted of a simultaneous determination of the solvent

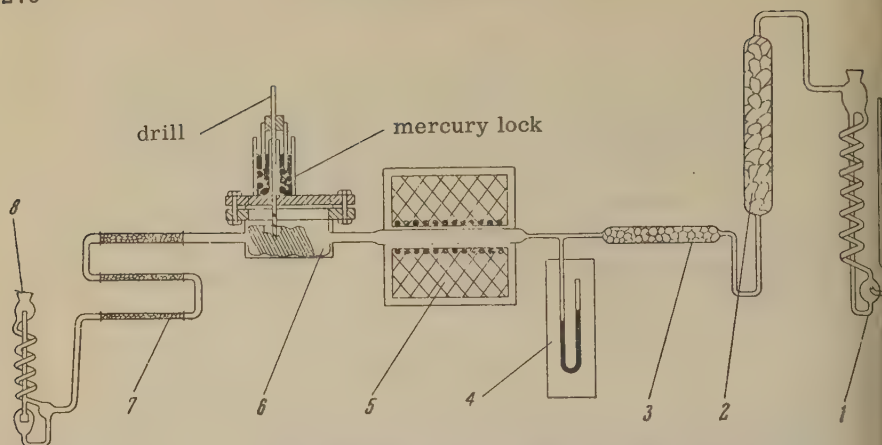


Fig. 1. Apparatus for simultaneous determinations of CO_2 and of H_2O in the inclusions: 1—absorber; 40% KOH; 2— CaCl_2 trap; 3—the "anhydron"; 4—mercury manometer; 5—resistance muffle; 6—plexiglass chamber (with the test crystal); 7—Pregl tubes; 8—absorber with $\text{Ba}(\text{OH})_2$.

water and of carbonic acid. Free carbonic acid was determined by the previously employed method for the determination of CO_2 in minerals and rocks [2]. The solvent water was determined by desiccation of the exposed cavity by a current of warm, dry, CO_2 -free air and by absorption of the moisture in Pregl tubes charged with anhydron (Fig. 1).

Air from the gasometer passing through absorber "1" containing 40% KOH, in order to purify it from carbon dioxide, was warmed to 35° to 40°C in a quartz tube placed inside the muffle "5". A mercury manometer "4" was placed between the anhydron and the quartz tubes, so as to control the air-tightness of the apparatus. The solvent water of the vacuole, while undergoing evaporation, was being transferred gradually from the plexiglass chamber "6" into the Pregl absorbing tubes "7". Carbon dioxide from the solution was absorbed by aqueous barite in the serpent-absorber "8" and was determined conductometrically.

The vacuole in the crystal was opened in the plexiglass chamber (Fig. 2), after the air-tight sealing and drying of this entire apparatus. Constant weight of the Pregl tubes served as the control.*

The vacuole was opened by a drill, $d \leq 1$ mm, previously inserted through the roof of the chamber. A mercury seal (Fig. 1) kept the apparatus air-tight. The drill was withdrawn from the crystal directly after the vacuole was opened in order to facilitate evaporation of the moisture. A prolonged aeration of the apparatus is required for a quantitative volatilization of the solvent water. In the case of the Gonchak crystal 1 (Fig. 3), the aeration was continued for 44 hours.

*I. e., in drying the sealed plexiglass chamber, the drying was continued until the weight of the H_2O -absorbers was constant. VPS

No appreciable amounts of free carbon dioxide could be found in the vacuole of this particular crystal.

After the complete evaporation of its moisture (to constant weight in the Pregl tubes), a small amount of CO_2 was recorded originating from decomposition of the bicarbonate.

After the chamber was dismantled, one could notice some visible traces of splashing of the solution: saline films on the inner surface of the chamber's lid, the surface of the crystal, and the drill were washed carefully with distilled water.

The inner walls of the vacuole were washed repeatedly by means of a micropipette. The entire solution was placed into a calibrated flask and was analyzed by the micro-analytical procedures. The Gonchak crystal 2 (Fig. 4) was examined in the same manner.

The volume of the vacuole, defined by the weight of water in the vacuole, was checked by M. N. Petrikova, the Laboratory of Ultra-microanalysis, by direct measurements of the volume of water required to fill the vacuole with the aid of an ultra-micropipette.

Analyses of the solutions in the Gonchak crystals 1 and 2 (Table 1) showed a



Fig. 2. Plexiglass chamber with drill, mercury lock, and test crystal.

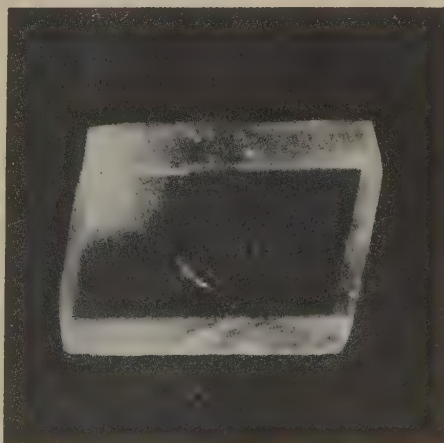


Fig. 3. Crystal with an inclusion used in the determinations of pH and SiO_2 (natural size).

Table 1. Chemical Characteristics of Liquid Inclusions in Crystals of Iceland Spar
from Deposits in the Siberian Platform

Lava beds				Tufogenic beds											
Constituent	Deposits in pillow lavas					Deposits in mandelstein		Deposits in the zone of fragmentation of tuffs				Deposits associated with the secant intrusions of trap rocks			
	Gonchak, crystal 1		Gonchak, crystal 2		Nidym, crystal 3	Spar, crystal 4	Yangurakta, crystal 5		Kuktule, crystal 6		Dzhekinde*		Markhal, *		
	mg	m equiv.	mg	m equiv.	mg	m equiv.	mg	m equiv.	mg	m equiv.	mg	m equiv.	mg	m equiv.	
HCO ₃ ⁻	0.19	0.003	a)	a)	a)	a)	a)	a)	a)	a)	a)	2.3	0.038	3.6	0.059
Cl ⁻	7.36	0.208	a)	a)	0.345	0.009	1.73	0.048	0.475	0.013	1.2	0.034	0.62	0.017	
SO ₄ ⁻	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)	a)
Sum	-	0.211	-	0.275	-	0.009	-	0.048	-	0.022	-	0.013	-	0.072	-
K ⁺	a)	a)	a)	a)	b)	b)	b)	b)	b)	b)	a)	a)	a)	a)	a)
Na ⁺	0.72	0.030	0.52	0.022	0.09	0.004	0.09	0.004	0.16	0.007	0.16	0.007	0.05	0.002	
Ca ⁺⁺	3.70	0.185	4.26	0.213	0.1	0.005	0.94	0.047	0.30	0.015	1.04	0.052	1.44	0.072	
Mg ⁺⁺	c)	-	c)	-	c)	-	c)	-	c)	-	c)	-	c)	-	-
Sum	-	0.215	-	0.235	-	0.009	-	0.051	-	0.022	-	0.008	-	0.059	-
Ca:Na ^{d)}	-	6.1	-	8.1	-	1.1	-	10.4	-	1.8	-	2.6	-	6.5	-
Dissolved salts } 136 grams per liter	230					74		158		72		47		-	
Hypothetical composition															
Ca(HCO ₃) ₂	0.25	-	-	-	-	-	-	-	-	-	-	3.05	-	4.66	-
CaCl ₂	9.93	-	11.82	-	0.28	-	2.60	-	0.83	-	0.33	-	0.78	-	0.72
NaCl	1.69	-	1.28	-	0.23	-	0.23	-	0.41	-	0.12	-	0.12	-	0.23
Volume of vacuole, mls	0.089		0.063		0.007		0.018		0.017		0.013		-		-

a) Not detected. b) Not determined. c) Higher than 0.0005 mg. d) Inconsistently calculated in the original. The ratios are as follows, left to right:
(m.e. Ca): (m.e. Na) 6.1; 9.7; 1.2; 11.7; 2.1; 3.0; 7.4; 36.0.
(mg. Ca): (mg. Na) 5.1; 8.2; 1.1; 10.4; 1.8; 2.6; 6.5; 28.8. VPS

*The composition of the solutions contained in the inclusions in the crystals of these deposits is characterized by aqueous extracts since the

very small concentration of carbonate in the first and absence of bicarbonate in the second crystal. Since the walls of the cavity consist of calcium carbonate, and the liquid in the vacuole should be at an equilibrium with this substance accordingly, any presence of the so-called aggressive carbonic acid in the solution needs be excluded as a possibility. Consequently, the amount of free CO_2 in solution cannot be higher than the amount representing that in equilibrium with the carbonate.

This proposition has made it feasible for us subsequently to dispense with the complicated direct measurement of carbonic acid in the liquid and in the gas contained in the vacuoles of the other crystals. Taking into account similarities in the volumes of the vacuoles, as determined by the two independent - VPS) methods, and considering the possible quantities of CO_2 in the solutions, as previously indicated, the second and the more simple variant of the procedure was followed in our studies of the other crystals.

Vacuoles in the crystals from Shpat, Indym, Kuktule, and Yangurakta are opened directly on the bench, without gravimetric determinations of water and CO_2 . In order to avoid possible splashing of the liquid, the vacuoles were drilled through the previously drilled plate of plexiglass. The solution was transferred by washing into a calibrated flask formerly. Volumes of the vacuoles were measured with the aid of an ultra-micropipette. The most common value, $f = 0.9^*$ was indicated by numerous measurements made by N. I. Andrusenko. For this reason, concentrations of the included solutions, in crystals 3, 4, 5, and 6 are calculated on the $f = 0.9$ basis. In the case of the Gonchak crystals (1 and 2), the concentrations were calculated on the basis of the gravimetrically determined solvent water.

Fairly noticeable quantities of bicarbonate and, consequently the equivalent quantities of calcium ion, were found in the filtered solutions, due to a certain solubility of calcium carbonate during the washing of the crystal (especially the solubility of the fine flour of calcite formed by the drilling). This magnitude of HCO_3^- was similar for all the crystals: 0.90, 0.90, 1.06, 1.05, 1.07 mm, for one and the same



Fig. 4. Crystal with a pierced vacuole (natural size - VPS).

* is the "degree of filling" which is 1, if the vacuole is 100% filled. VPS

volume, and was very close to the solubility of CaCO_3 in water, under conditions of our operations with the crystals. It became necessary, therefore, to eliminate this HCO_3^- magnitude from the analyses and to subtract the equivalent quantity of calcium from the determined quantity. As the result, it became evident that the concentration of bicarbonate is insignificant in many inclusions, with the exception of crystals 1, 7, and 8. The somewhat higher content of HCO_3^- is characteristic of the extracts of the Markhaya and the Dzhekinde crystals.

Analyses of the solutions of the inclusions in eight crystals are summarized in Table 1.

CHARACTERISTICS OF INCLUSIONS AND CONSIDERATIONS REGARDING THEIR ORIGIN

The specific feature of the inclusions in Iceland spar is the fact that the liquid inclusions in many crystals proved to be of the calcium-sodium-chloride composition. Concentrations of these solutes are fairly high in many inclusions. There is no visible relationship between the Ca:Na ratio and the kind or composition of inclusions in crystals from deposits of different types. This ratio varies from 1 to 8 in solutions within inclusions in crystals of one and the same genetic type, as, for example, in crystals from the pillow lava deposits of Gonchak and Nidym. The range of variation in the Ca:Na ratio is from 1 to 10.4 for all types of the deposits. Only in the Markhal deposit does this ratio go up to 28, because of the preponderance of calcium bicarbonate in the solution. The concentration of total salts in the liquid phase of the inclusions we studied ranges from 47 to 231 grams per liter. High salinity is found in the Gonchak and the Shpat crystals. In the latter case, the solutes are 90% CaCl_2 , with total salts of 158 grams/liter.

Two of the Gonchak crystals, with vacuoles, were used especially for measurements of the pH of the media. These measurements gave the pH of 5 to 5.5, by the universal indicator.

The small amounts of carbonic acid, the high concentrations of chlorides, and the preponderance of calcium chloride in the inclusions in Iceland spar from many deposits in the Siberian Platform are indicative of the specificity and of the singleness of the fundamental process by which the environmental characteristics of the deposition of the spar were determined for the Siberian Platform.

According to the results by E. Ya. Kievlenko, the paragenetic associations of minerals are typically hydrothermal, for the crystals we studied. Moreover, the calcite mineralization was accompanied by a wide assemblage of zeolites and was associated with the low-temperature stage of the process as a whole.

General geologic premises and the mineral associations are indicative of the post-volcanic nature of the basic process in which both chlorides and carbonic acid were participating, judging by the

composition of the solutions captured in the vacuoles. There may have been accessions of both carbonic acid and chlorides associated with water vapor, as exhalations, during the stage of the volcanic process, as here visualized. Also, one may assume the possibility of formation of hydrogen chloride by interaction between hot streams of lava and chloride-bearing waters (for example in the case of pillow lavas).

The initial stage of this process must have been accompanied, first of all, by the appearance of sodium in solution as the result of an interaction between carbonic acid and, possibly, of hydrogen chloride with the tuffaceous and the lava materials.

The appearance of dissolved sodium had accelerated the solution of calcium. The formation of calcium chloride has led, in turn, to further displacements of sodium into the solution. Such exchanges were going on in various ways in different micro-areas (fissures, cavities) and they were accompanied by a deposition of zeolites with widely different calcium-sodium ratios. This view of the phenomena that could have been taking place in the process may be illustrated further by the data in the Table reporting the experimental findings that have a bearing on the interactions between aqueous solutions of sodium and calcium chloride and the diabasic gabbro from the Dzhekinde deposit. The experiments were conducted at somewhat elevated temperatures and pressures, in order to secure a clearer expression of the differences in the chemistry of the end-solutions resulting from reactions between water and the different solutes with the rock.

The experiments were set up in a flowing-water reactor in the cavity of which 3 to 5 mm fragments of the rock were placed. The water and the solutions were flowing at a constant rate through the cavity containing the charge, under pre-determined conditions. The products of the reaction, after their passing through the condenser, were collected in special vessels for the analysis.

The diabasic gabbro used in the experiments had the following mineralogic composition: 40 to 50% plagioclase (labradorite No. 56-0); 35 to 40% monoclinic pyroxene; 5% olivine; 5% titaniferous magnetite; 3% sphene and apatite.

Chemical composition of the solutions resulting from the interactions between the diabasic gabbro and the water or the aqueous chlorides, at 300°C and at 87 atm. pressure, is shown in Table 2. Four hours were allowed for the interaction.

Table 2

Medium	Found in solution, milligrams per liter						
	SiO ₂	Al ₂ O ₃	Fe ⁺⁺⁺	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
H ₂ O	193	34	1	23	13	0.8	0.1
1 N NaCl	203	24	1	not dtd.	25	119	0.1
1 N CaCl ₂	162	26	2	99	22	not dtd.	0.1

As we may see from the experimental results, the main effect of dissolved sodium and calcium chlorides is the displacement of one cation by another, whereupon their totals increase in the solution.* This effect is weaker, in the case of potassium, and the potassium content of the rock is low, in any case.

Silica, alumina, calcium, and sodium are the principal constituents of the rock that pass into solution. Paragenetic association of the minerals, consisting chiefly of zeolites and calcite, suggests relatively low temperatures of the solutions and their resemblance to the solutions used in the experiments, in respect to their composition. Observations of solutions obtained by reactions of water or aqueous electrolytes with granitoid rocks and with certain effusive rocks indicate that the temperature range for the fixation of zeolites is at 200°C and still lower.

The experimental results obtained at 300°C and 87 atm. pressure would remain qualitatively significant also at the less drastic temperatures and pressures, in the environment where the general relationships between the solutes would be essentially the same. The results obtained at 300°C and 87 atm. serve merely to emphasize the predominance of SiO_2 , Al_2O_3 , Ca, Na as the main participants in the process and of their accessions from the rocks to the solutions.

The following constituents were present accordingly in the solutions circulating in the tectonically disturbed zones: CO_2 , HCO_3^- , Cl, Ca, Na, Al_2O_3 , SiO_2 . Their concentrations were increasing progressively with the advancing movement of the solutions, which was conducive to a deposition of aluminosilicates, the zeolites containing water, Na, and Ca, in the thermally favorable zones of the rock. As the result, only Ca^{2+} , Na^+ , Cl^- , HCO_3^- , and CO_2 remained in the solutions. In the environment of a relatively confined system, the presence of dissolved NaCl and CaCl_2 was conducive to the decomposition of CaCO_3 , at a certain depth from the surface.

The probability of this phenomenon was sustained by the studies of reactions of marmorized limestone with water or with aqueous solutions of sodium and calcium chlorides carried out in a manner analogous to the experiments with diabase. Table 3 shows the amounts of calcium carbonate decomposed by the interaction of marble with water and with the solution of sodium and calcium chlorides.

The entire system passes from the relatively confined state into the unconfined, in the upper parts of the deposit. The gaseous constituent of the solution—the carbonic acid—tends to escape for that reason, and the equilibrium becomes shifted in the direction conducive to the formation of calcite. The regular shape of the crystals suggests a quiet and gradual withdrawal of the carbonic acid.

Both the mineral associations accompanying Iceland spar and the numerous thermometric studies by N. I. Andrusenko indicate that the

*This statement is not easily harmonized either with the stoichiometry of the exchange or with the figures in Table 2. VPS

Table 3

T	P	Amount of decomposed CaCO_3 after 4 hours of interaction with marble, mg per liter	
		with H_2O	with 0.25 N NaCl plus 1N CaCl_2
300	87	36	107
400	200	92	435

position process takes its course at temperatures below 200°C . As the pressures—they may be estimated from the following considerations.

The degree of filling of most inclusions is close to 0.9. Since many the solutions are high in sodium and calcium chloride, we should expect a certain lowering of their vapor pressure, as against the vapor pressure of water. S. D. Malinin had performed certain measurements especially to ascertain the vapor pressures of solutions resembling the inclusions in their composition. The curves in Figure 5 show measured vapor pressures of sodium and calcium chloride solutions at total concentration of grams per liter and with Ca:Na ratio of 4, as against the vapor pressure of pure water determined in analogous environments. As seen in Figure 5, the curves differ noticeably only above 245°C , at the degree of filling here assumed. The two curves coincide below this temperature. It appears, therefore, that the pressures at which the deposition of calcite was taking place were probably not very different from the vapor pressure of water, at the saturation, and did not exceed 16 atmospheres at 200°C and below. Environments at pressures only slightly higher than the atmospheric pressure must have been the most commonly preponderant ones. The presence of excess CO_2 (as against the equilibrium concentration)

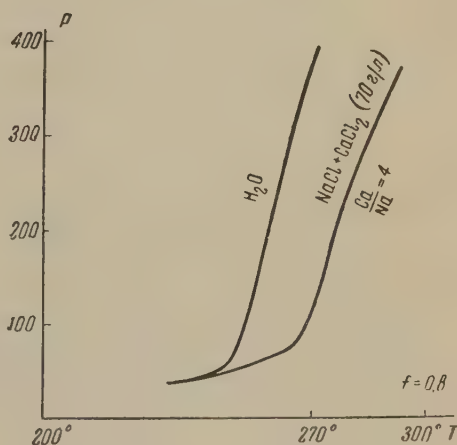


Fig. 5. The pressure curve for NaCl- CaCl_2 solution in reference to vapor pressure curve for pure water.

and the perfect form of the crystals may be taken as a confirmation of this surmise. Perfection of the crystals is an indication of the quiet evolution of the CO_2 , as has been pointed out previously.

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THE PROBLEM OF THE RELATIVE ABUNDANCE OF SCANDIUM IN WOLFRAMITES

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Abstract

The distribution of scandium in wolframites of various rare metal deposits has been studied. On the basis of 450 quantitative spectral analyses of wolframites from 47 deposits, it has been established that: 1) As a rule, higher scandium concentrations (0.02—0.2 per cent of Sc_2O_3) are found in wolframites from high-temperature pneumatolyto-hydrothermal greisen type deposits. 2) The scandium content in wolframites from pneumatolyto-hydrothermal deposits (0.04 per cent of Sc_2O_3) is at least an order higher than in wolframites from low-temperature hydrothermal deposits (0.002 per cent of Sc_2O_3). In a large number of wolframite specimens from low-temperature quartz veins (often with pyrites) scandium has not been detected. It has been found that scandium usually concentrates in wolframites and ferrihydrites (up to 0.2 per cent of Sc_2O_3), whereas hübnerites have lower scandium contents (up to 0.02 per cent of Sc_2O_3).

Scandium is a typical dispersed element. It is present in all principal types of igneous rocks in insignificant quantities (0.001 to 0.01% Sc_2O_3), where its bulk is localized in the dark minerals. Only two independent minerals of scandium are known so far: thortveitite and bazzite, both of which are extremely rare. For this reason, scandium-bearing minerals are especially interesting, inasmuch as they contain accumulations of scandium (up to 0.1 to 1%). Wolframite is one of such minerals; its scandium content may be as high as tenths of one per cent.

The presence of scandium in wolframites was first established by Eberhard [8]. R. Meyer, in 1908 [10], showed that scandium may be present in appreciable quantities in wolframite and he isolated scandium oxide from wolframite tailings. V. M. Goldschmidt discovered, in 1931 [3], that the wolframites of the Zinnwald contain up to 0.1% Sc_2O_3 . He suggested also that scandium replaces divalent iron isovalently in wolframite, in the form of ScNbO_4 or ScTaO_4 . Leutwein, in 1951 [9], studied wolframites of the Zinnwald (Rudnyy) and of some other deposits. He concluded that the substitution of ScNbO_4 for FeWO_4 in wolframite is thermodynamically impossible. In 1955, H. Schrocke [11] demonstrated the presence of scandium in

wolframites from certain deposits in Europe, Asia, South America, and Australia.

Beginning with 1953, the relationships involved in the distribution of scandium in wolframites are being studied at the Institute of Mineralogy, Geochemistry and Crystal-Chemistry of the Academy of Sciences of the USSR (the IMGRE, ANSSSR).

The investigation of wolframites at the IMGRE showed that scandium anomalies are found generally in pneumatolytic-hydrothermal deposits of the high-temperature greisen type. In the territory of the USSR, such deposits are known in central Kazakhstan (Akchatau, Bainazar, Maitas), in Eastern Transbaikal (Sherlova Gora), and in the northeast of Asia (Polyarnoe).

These deposits are related genetically to intrusions of acid magma. The magmatic rocks are represented generally by leucocratic granites of the alkali-rich group of ultra-acid and acid rocks. Their age is Varisca, in central Kazakhstan and in the northeast of Asia.

Scandium-bearing greisens are associated with the apical parts of small intrusions, as a rule, or with the apophyses of large intrusions, and are situated generally in the granite-host rock contact zones. They are found chiefly in rocks of the granitic bodies themselves (Akchatau, Sherlova Gora, Polyarnoe) and, more rarely, in the rocks of the roof (Bainazar).

Greisen bodies with scandium-bearing wolframite have generally complex structures consisting of greisen-proper (formed by alterations of the host rocks) and of vein fillings where the principal vein mineral is quartz. The contact between these two parts of the greisen is generally fairly well defined (Figs. 1 and 2).

The shape of the ore bodies is represented mainly by two varieties: a) Vein-like bodies, fairly consistent in their length and dip (generally steep). Such bodies may be up to 1 to 2 km long and up to tens of meters thick (Akchatau, Kara Oba, Polyarnoe). b) Stockworks of veins in which one or several systems of quartz veins and minute veinlets form a complicated network in the greisen body (Bainazar). The plane projection of such bodies resembles a circle with the area that may be as large as several hundred square meters. Such ore bodies wedge-out fairly rapidly in depth but they may also reappear.

The mineralogic composition of greisens is as follows:

- a) The principal minerals: quartz, muscovite, topaz, beryl, fluorite, tourmaline.
- b) The ore minerals: pyrite, wolframite, cassiterite, molybdenite, bismuth minerals, arsenopyrite, scheelite, hematite, pyrrhotite, galena, and others. Scandium-bearing greisens contain, on the average, about 70% quartz, about 20% topaz and fluorite, and up to 40% muscovite; beryl and ore minerals are present.

The invariable preponderance of quartz, the prominence of the fluorine minerals (topaz and fluorite), and the appreciable role of beryl are among the most characteristic mineralogic features of greisens in which the scandium-bearing minerals are also present.

Scandium-bearing wolframite is found in the bodies of replacement, as well as in the fissure-filled veins. In the former it forms generally small inclusions (up to 1 mm in diameter) (Fig. 1); in the latter it forms fairly large platy crystals (up to 10 to 15 cm long). Concentrations of scandium in wolframites from greisen and from vein fillings are about the same. There is generally no scandium in the

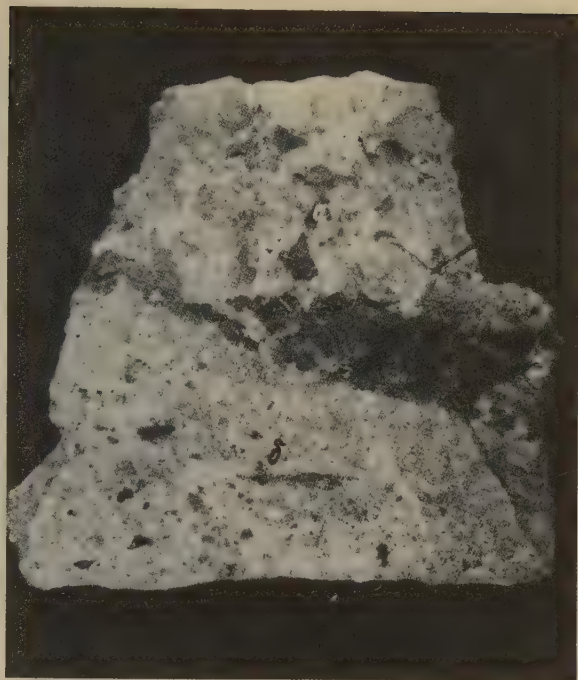


Fig. 1. Contact between vein filling (a) and greisen (b).

medium-temperature wolframite deposits represented by quartz veins (often with sulfides) and by weakly greisenized host rocks, or else the amounts of scandium are appreciably smaller than in high-temperature wolframites, not exceeding 0.02% Sc_2O_3 , as a rule.

We examined nearly 450 samples of wolframite from 47 different deposits. Carefully selected pure samples of wolframite were taken for the analysis. Scandium was determined quantitatively, by comparison of the spectra with the photometric aid (densitometer? VPS). About 20 mg of the sample was burned in the arc. The current was $\pm 2\text{a}$. at 220 v pressure, at the time of photographing of the spectra. Sensitivity of the method is about 0.005% (Sc metal). Reliability of the method is $\pm 15\%$. Scandium was determined by the 2552.359 \AA line.

The results indicated the presence of scandium anomalies (0.02 to 0.043% Sc_2O_3) in wolframites from high-temperature rare metal deposits of the pneumatolytic-hydrothermal type (Table 1), with an average of 0.043% Sc_2O_3 (the majority of wolframites from hydrothermal deposits showed a complete absence of scandium). Thus scandium anomalies in wolframites are associated with the transition from pneumatolytes to hydrotherms.

The highest content of scandium was found by us in a wolframite from the Akchatau pegmatitic deposit. It should be noted, however, that wolframite is extremely rare in these pegmatites and that it does not form any appreciable accumulations. For this reason, the following discussion is concerned chiefly with wolframites from pneumatolytic-hydrothermal and hydrothermal deposits.

Tables 2 and 3 give a comparison between the scandium content of wolframites from pneumatolytic-hydrothermal and from some especially typical hydrothermal deposits. The average minimum for the pneumatolytic-hydrothermal wolframites is 0.027% Sc_2O_3 ; the average maximum—0.068% Sc_2O_3 . The Sc_2O_3 minimum for hydrothermal wolframites is zero; the average maximum—0.011% Sc_2O_3 .

The Kara Oba wolframites, with the average of 0.02% Sc_2O_3 , are representative in this connection. The Kara Oba wolframites from the clearly greisenized high-temperature ore bodies contain, on the average, 0.028% Sc_2O_3 , whereas wolframites from the low-temperature quartz veins contain no scandium as a rule. Similar relationships in



Fig. 2. Wolframite in quartz of vein filling (a) and in greisen (b).

Table 1. The Average Content of Sc_2O_3 in Wolframites from Different Rare Metal Deposits of the USSR

Type of deposit	Number of samples examined	Average Sc_2O_3 in wolframite	Number of deposits	Representative deposits
Pneumatolithic-hydrothermal	234	About 0.043	12	Akchatau; Bainazar; Sherlova Gora Antonova Gora; Dedova Gora; Kolyvan
	232	About 0.002	34	

Table 2. Sc_2O_3 Content of Wolframites in Pneumatolytic-Hydrothermal Deposits

Deposit	Number of determinations	Sc_2O_3 , %		Average
		Minimum	Maximum	
Kara-Oba	50	Not detected	0.07	0.02
Maikul	2	0.02	0.02	0.02
Maitas	3	0.03	0.03	0.03
Akchatau	120	0.005	0.12	0.055
Sherlova Gora	15	0.005	0.07	0.049
Iultin	2	0.05	0.05	0.05
Bainazar	11	0.01	0.075	0.059
Zhannet	4	0.05	0.08	0.062
Polyarnoe	22	0.07	0.1	0.076
N. Kounrad	9	0.005	0.07	0.024

the behavior of scandium were reported by A. S. Dudykina* for castorites of different origin.

Table 4 shows the average scandium in the Akchatau wolframites from greisen and vein fillings. Wolframites from the quartz-topaz greisen contain 0.033% Sc_2O_3 ; wolframites from the quartz vein fillings—0.033% Sc_2O_3 . Variations in the scandium content of wolframites from different parts of one and the same ore body (the greisen and the vein fillings) are not appreciable therefore and do not exceed 0.01% Sc_2O_3 .

The content of scandium in a wolframite is affected significantly by the chemical composition of the mineral, as well as by the character

Table 3. Sc_2O_3 Content of Wolframites from Hydrothermal Deposits

Deposit	Number of determinations	Sc_2O_3 , %		Average
		Minimum	Maximum	
Aldakachan	7	Not detected	Not detected	-
Dedova Gora	7	Not detected	Not detected	-
Kolyvan	7	Not detected	Not detected	-
Antonova Gora	22	Not detected	0.005	0.0006
Belukha	16	Not detected	0.01	0.001
Bukuka	29	Not detected	0.05	0.0025

* S. Dudykina. Geokhimicheskie Zakonomernosti Raspredeleniya Scandiya v Mineral i Gornyykh Porodakh SSSR (Geochemical relationships in the distribution of scandium in minerals and rocks of the USSR). 1953 (Manuscript). Library of Sciences, USSR.

of the deposit. Chemical and spectrographic analyses of wolframites from different rare metal deposits of the USSR showed that there is more scandium in wolframites and ferberites, as a rule. These analyses were done at the Institute of Mineralogy, Geochemistry and Crystal-Chemistry of Rare Metals, and at the Moscow Institute of Fine Chemical Technology (Table 5).

In huebnerites, however, scandium is either completely absent, as a rule, or does not exceed 0.02% Sc_2O_3 . We may be dealing here with the phenomenon noticed already by A. E.

Fersman: autolysis—self-purification.

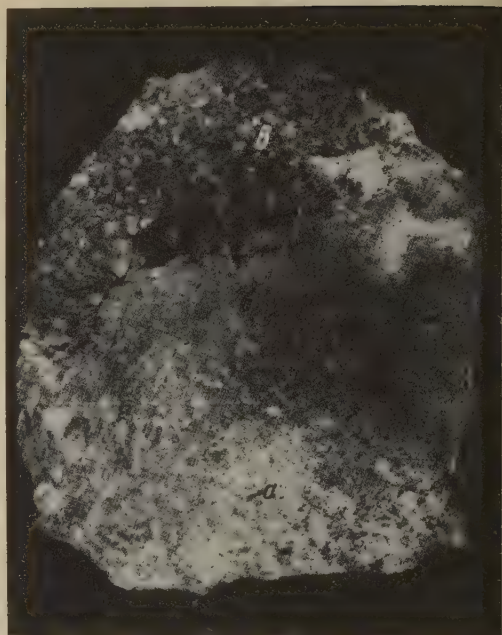


Fig. 3. Zonations in a greisen vein body. (a) -greisenized granite; (b) -quartz greisen; (c) quartz-muscovite greisen.

Table 4. Sc_2O_3 Content of Wolframite from Different Parts of Ore Body

% Sc_2O_3 in wolframites from quartz-topaz greisen				% Sc_2O_3 in wolframites from quartz veins fillings			
Number of determinations	Min.	Max.	Average	Number of determinations	Min.	Max.	Average
8	0.01	0.095	0.033	21	0.02	0.1	0.042

The maximum scandium content in minerals of the wolframite group is given in Table 6. The amount of scandium in these minerals decreases with decrease in divalent iron and their electronegativity and with increase in the ionic radii.

Table 5. Sc_2O_3 Content of Wolframites in Relation to their Composition

Constituent	Sample no. †						
	1056	1013	977	467	1118	911	610
Sc_2O_3 *	0.07	0.07	0.1	0.1	0.07	0.07	0.07
FeO †	12.58	10.52	12.82	14.11	12.30	13.04	22.64
MnO †	11.90	14.79	11.47	9.74	12.27	10.64	2.56
WO_3 †	75.75	74.99	75.66	76.28	75.56	76.18	75.28

Spectrographically; N.V. Lizunov, Analyst.

Chemically; P.V. Diomidova and I.A. Bogdanovich, Analysts.

1056-Akchatau, Greisen Stock 1; 1118-Akchatau, Vein 6;

1013- " , Vein 147; 911- " , " 152;

977- " , " 73; 610-Sherlova Gora.

467- " , " 14;

Table 6. Sc_2O_3 in Tungsten Minerals. Maximum Concentrations.

Mineral	Sc_2O_3 max. %	Composition, %		Cation *	
		FeO	MnO	ri, Å	E., kcal
ferberite, WO_4	0.1 to 0.02	23.6 to 18.9	0 to 4.7	0.74	185
wolframite, (Fe,Mn) WO_4	0.1 to 0.2	18.9 to 4.8	4.7 to 18.7	0.74; 0.8	185; 170
hübnerite, WO_4	up to 0.02	4.8 to 0	18.7 to 23.4	0.8	170

e., Fe or Mn; ionic radii are meant by the "r i". VPS

CONCLUSIONS

1. Scandium anomalies (0.02 to 0.2% Sc_2O_3), as a rule, are formed in wolframites in pneumatolytic-hydrothermal deposits of greisen

2. The average content of scandium in wolframites from pneumatolytic-hydrothermal deposits (0.04% Sc_2O_3) is greater, by at least one order of magnitude, than it is in wolframites from low-temperature hydrothermal deposits.

3. Scandium is accumulated generally in wolframites and ferberite (up to 0.2% Sc_2O_3) but is found in much smaller amounts in hübnerite (up to 0.02% Sc_2O_3).

Finally, the authors take this opportunity to express their particular thanks to L. N. Komissarova, for her aid in the analyses for the present publication.

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RARE AND DISPERSED ELEMENTS IN SKARNS OF TYRNY-AUZ [SOVIET ARMENIA]

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Abstract

Distribution and behavior of the major and 12 minor elements in skarns of Tyrny-Auz, Soviet Armenia, are investigated from the standpoint of changes in rock and specific mineral composition. The minor elements studied are tin, manganum, gallium, cobalt, nickel, chromium, vanadium, titanium, zirconium, strontium, barium, and beryllium. The skarn zone occurs in an anticline along a biotite hornfels-marble contact; the hornfels is 80 per cent skarnized, the marble 10 per cent. In sequence of increasing alteration, skarn zones in the biotite hornfels are amphibole-biotite hornfels, pyroxene hornfels, and garnet pyroxenites; skarn zones in the marble are vesuvianite-wollastonites and garnet or non-garnet pyroxenites. Skarnization of the hornfels produced marked increase in Fe, Mn, Ca; decrease in Al and Ti; and almost complete removal of alkalis. Skarnization of the marble resulted in increase in Si, Ti, Al, Fe, Mg, and Mn. Only Fe and lesser amounts of Mn are believed to have been carried in by solution; gains and losses of other major elements are caused by redistribution of the elements within and within the original rocks present. Of the minor elements, only Sn and smaller amounts of Ge are believed to have been brought in by solution. Ga, Co, Cr, V, Ti, Zr, Sr, Ba, and Be were abstracted from the biotite hornfels and redistributed during skarnization. Cr, V, Ti, Zr, Sr, and Ba were withdrawn from the hornfels faster than Ni, Ga, Co, and Be are derived from the hornfels at a perceptibly perceptible rate. Chemical analyses are given for major and the 12 minor elements in biotite hornfels, marble and their respective skarns. The abundance of Cr, V, Ti, Sr, and Ba in the skarn minerals biotite, plagioclase, pyroxene, garnet, wollastonite, and vesuvianite and Ge, Sn, Co, and Ni in these minerals as well as in pyrrhotite, pyrite, chalcopyrite, and sphalerite indicates to what degree these elements isomorphously enter the crystal structure of silicates and sulfides.

Distribution and behavior of tin, germanium, gallium, cobalt, nickel, chromium, vanadium, titanium, zirconium, strontium, barium, and beryllium in the process of development of a skarn deposit are discussed in the present article. These rare and dispersed elements were determined at the Spectrographic Laboratory of the Vernadskii Institute. Tungsten and molybdenum, the chief ore elements, are omitted from the discussion.

The most recent data on geologic structures of the Tyrny-Auz pre-skarn formation of a skarn zone, wherein ore is contained in an anticline fold along a stratigraphic contact between marble and biotite hornfels [1]. Thickness of the skarns is irregular, with a maximum

thickness up to 100 meters and more in the apex of the anticline. Depth of the skarn deposit has been traced down to 800 meters.

Formation of the skarns, as a whole, may be visualized as follows: The solutions, while moving along the biotite hornfels-marble contacts, replaced both of these rocks, so that 80% of the skarns are in hornfels and 20% in marble.

As a result, the following zoned "hornfels" skarn developed: a) biotite hornfels; b) amphibole-biotite hornfels; c) pyroxene hornfels; d) pyroxene-garnet and garnet-pyroxene skarns.

Zoned skarns in the marble (the "limestone" skarns) have a somewhat different appearance: a) marble; b) vesuvianite-wollastonite skarns; c) pyroxene and pyroxene-garnet skarns. In many places some of these zones fail to develop, whereupon the zoned sequence of skarns is truncated. We should point out that the zoned pattern here proposed should be taken less in a structural than in a genetic sense.

As a rule amphibole-biotite hornfels in the contact between the biotite and pyroxene hornfels forms a narrow band (a few centimeters across) and may be identified only by microscopic studies. In some isolated cases, the vesuvianite-wollastonite skarns are prominently developed in the deposit, although generally speaking their role is insignificant in skarn-formation. The bulk of the deposit consists of pyroxene hornfels, pyroxene, and pyroxene-garnet skarns.

Chemical features of the alteration of biotite hornfels to its metasomatic end-product, the pyroxene-garnet skarns, are presented in Table 1. The analyses show a conspicuous increase in Fe, Mn, and Ca, in skarnization, with a concurrent decrease in Al and Ti, and a

Table 1

Constituent	Rock			
	Biotite hornfels* (01040)	Biotite hornfels**	Pyroxene-garnet skarn (01031)	Pyroxene-garnet skarn (01073)
	%	%	%	%
SiO ₂	58.20	54.05	51.21	46.72
TiO ₂	0.70	0.87	0.17	0.30
Al ₂ O ₃	18.70	23.85	5.83	7.29
Fe ₂ O ₃	2.53	1.62	4.19	8.30
FeO	5.17	3.45	11.85	7.47
MnO	trace	trace	0.99	0.96
MgO	1.60	0.88	2.76	0.64
CaO	2.43	6.10	23.03	29.18
K ₂ O+Na ₂ O	*	8.62		
Loss on ignition	2.2	2.48		

*Probably around 8½% alkalis; value omitted in original.

**No identification number given in original.

practically complete removal of alkalis. Skarnization of marble is accompanied by increase in Fe, Mn, Al, Mg, Ti, and Si (Table 2). The results demonstrate significant accessions of Fe and somewhat smaller amounts of Mn from the skarn-forming solutions. The other elements are only redistributed between the marble and biotite hornfels according to bimetasomatic exchange. Ca is transferred from the marble to the hornfels, where it is essential in the formation of "hornfels" skarns. In turn, Al, Mg, and Si are transferred from the hornfels to the marble where they contribute to the formation of "limestone" skarns.

Mineralogic composition of the altered rocks varies, depending on the intensity of the skarn-forming process. Biotite hornfels, represented by biotite, quartz, potassium feldspar, and plagioclase, is replaced by the amphibole-biotite hornfels, with accompanying decomposition of biotite and potassium feldspar. Potassium is withdrawn from the rock, while the elements of which the biotite was composed are constituted as amphibole, with some incompletely decomposed biotite flakes still present in the rock. A more thorough reworking of the biotite hornfels leads to formation of pyroxene hornfels, with characteristic mineralogic association of pyroxene, quartz, and plagioclase. The end-product of the most thorough altered biotite hornfels—pyroxene-garnet and garnet-pyroxene skarns—consists of pyroxene, garnet, quartz, and definitely subordinate amounts of plagioclase. In some cases the amounts of quartz fluctuate within a wide range. The principal rock-forming minerals of skarns—pyroxene and garnet—belong respectively to the diopside-hedenbergite and the grossularite-transterite series.

Vesuvianite-wollastonite and pyroxene-garnet skarns form by replacement of marble. They are represented respectively by vesuvianite with wollastonite and by pyroxene with garnet, together with small amounts of quartz.

Grossularite is locally present in appreciable quantities, especially in limestone skarns.

Of all altered rock types considered, we succeeded in isolating single-mineral fractions of pyroxene, garnet, plagioclase, vesuvianite, and wollastonite only from pyroxene-garnet, garnet-pyroxene-plagioclase, and

Table 2

Constituent	Rock	
	Marble (01041)	Pyroxene-garnet skarn (01187)
	%	%
SiO ₂	2.95	42.72
TiO ₂	0.03	0.12
Al ₂ O ₃	3.66	4.04
Fe ₂ O ₃	0.78	9.20
FeO	0.7	13.51
MnO	trace	2.17
MgO	1.64	0.65
CaO	51.50	26.65
K ₂ O+Na ₂ O	-	-
Loss on ignition	38.12	-

vesuvianite-wollastonite skarns. These fractions were analyzed for rare and dispersed elements in our study of the distribution of these elements in different minerals. Amphibole-biotite and pyroxene-hornfels have fine-grained textures, and it was not possible, for that reason, to obtain single-mineral fractions of sufficient purity from them. These latter rocks were therefore characterized only by total analyses. We succeeded in isolating and analyzing only biotite from the biotite hornfels.

In addition to silicate skarn minerals, the sulfides—pyrrhotite, pyrite, chalcopyrite, and sphalerite—also were examined for dispersed elements. Sulfides, as lenses and disseminated ores, replace skarns in the final stage of formation of the deposit. Their analysis is important relative to influx of elements during the sulfide stage.

Quartz-molybdenite mineralization occurring in stockworks which followed skarn mineralization in pre-sulfide stages has no bearing on skarnization and is therefore not considered.

Distribution of rare and dispersed elements in different types of skarns (Table 3) shows abrupt increases of tin and, to a lesser extent, of germanium in the skarns as compared with the original rocks. Content of the other elements decreases regularly, on the whole, from the biotite hornfels to marble. Consequently, we may definitely consider the influx of only these two elements. The others are merely transferred from the biotite hornfels to the skarns in a replacement process with accompanying losses of chromium, vanadium, titanium, zirconium, strontium, and barium from the skarns. The losses of nickel are less conspicuous. There are practically no losses of gallium, cobalt, and beryllium under the same conditions. Accession and precipitation of rare and dispersed elements in the "limestone" skarns

Table 3

Element	Skarns in biotite hornfels (hornfels skarns)			Skarns in marble ("limestone" skarns)		
	Biotite -hornfels (average of 33 samples)	Pyroxene -hornfels (average of 82 samples)	Pyroxene -garnet skarn (average of 75 samples)	Pyroxene -garnet skarn (average of 41 samples)	Vesuvianite- wollastonite skarn (average of 28 samples)	Marble (average of 29 samples)
	%	%	%	%	%	%
Ge	-	-	0.001-0.003	0.001-0.005	<0.001	-
Sn	0.001-0.003	0.003-0.008	0.01 -0.05	0.01 -0.05	0.003-0.005	-
Ga	0.001-0.005	0.001-0.005	0.001-0.005	0.001-0.005	0.001	-
Co	~0.001	~0.001	~0.001	~0.001	-	-
Ni	0.003-0.008	0.003-0.008	0.001-0.005	0.001-0.003	0.001	-
Cr	0.005-0.01	0.005-0.01	0.003-0.005	0.001-0.005	0.001	<0.001
V	0.005-0.01	0.005-0.01	0.003-0.008	0.003-0.008	0.001-0.003	-
Ti	0.8 -0.9	0.5 -0.6	0.3 -0.4	0.2	0.03 -0.05	-
Zr	0.01 -0.05	0.008-0.03	<0.001	<0.001	0.003	-
Sr	0.1 -0.5	0.1 -0.5	0.01 -0.05	0.01 -0.05	0.005-0.01	0.1 -0.8
Ba	0.03 -0.1	0.008-0.03	0.001-0.005	0.003-0.005	0.001	0.001-0.003
Be	0.001-0.003	0.001-0.003	0.001-0.003	0.001-0.003	0.001	-

place in the order of bimetasomatic exchanges between biotite hornfels (from which the elements are withdrawn) and the marble, very much like the case of the principal petrogenic elements, aluminum, magnesium, and silicon in formation of "limestone" skarns (Table 4). Characteristically, elements such as chromium, strontium, and barium apparently had appreciable mobility, during skarnization, being transferred to the marble where they were commonly deposited in appreciable quantities (i.e. strontium). This problem remains to be studied in detail, however, and we do not exclude the possibility of accumulation of these elements during formation of limestone skarns.

Let us consider now the behavior of specific rare and dispersed elements in the formation of a skarn deposit.

Tin and germanium are present in all silicate skarn minerals. They are conspicuously high in garnets. Moreover, whereas garnet is practically the sole accumulator of germanium and only traces of germanium are found in the other minerals, appreciable quantities of tin are found in several skarn minerals (Table 5). The ions, Ge^{4+} and Sn^{4+} , probably follow silicon, Si^{4+} , in skarnization, and replacing silicon in silicate crystal structures [2]. The abrupt increase of Ge and Sn in skarns versus the original rock is a definite indication of

Table 4. Inflow and Outflow of Principal Ore-Forming Elements and Rare and Dispersed Elements During Formation of Skarns

	Elements			
	Outflow		Inflow	
	Major	Rare and dispersed	Major	Rare and dispersed
Hornfels skarns	Si^{4+} Al^{3+} Mg^{2+} K^+ Na^+	Ga^{3+} Co^{2+} Ni^{2+} Cr^{3+} V^{3+} Ti^{4+} Zr^{4+} Sr^{2+} Ba^{2+} Be^{2+}	$\text{Fe}^{2+} + \text{Fe}^{3+*}$ Mn^{2+*} Ca^{2+}	Ge^{4+*} Sn^{4+*} $\text{Co}^{2+}(?)^*$ $\text{Ni}^{2+}(?)^*$
Lime skarns	Ca^{2+}		Si^{4+} Al^{3+} $\text{Fe}^{2+} + \text{Fe}^{3+*}$ Mg^{2+} Mn^{2+*}	Ge^{4+*} Sn^{4+*} Ga^{3+} Co^{2+} Ni^{2+} Cr^{3+} V^{3+} Ti^{4+} Zr^{4+} Sr^{2+} Ba^{2+} Be^{2+}

*By accession from skarn-forming solutions.

Table 5

Mineral	Number of analyses	% Ge	% Sn
Biotite	4	-	-
Plagioclase	8	-	-
Pyroxene	15	0.001	0.01
Garnet	27	0.004	0.2
Wollastonite	15	-	0.001
Vesuvianite	13	0.001	0.15
Pyrrhotite	13	-	0.02
Pyrite	7	-	0.08
Chalcopyrite	5	-	0.003
Sphalerite	6	-	0.01

in garnet; 0.007% in plagioclase; 0.004% in vesuvianite; < 0.001% in pyroxene. Gallium is absent in wollastonite and in sulfides.

Gallium "highs" in plagioclase, garnet, and vesuvianite show its direct association with aluminum (the ionic radii of Ga^{3+} and Al^{3+} are 0.62 and 0.57 Å respectively). In the original rocks (biotite hornfels) gallium is associated with feldspars and biotite. During skarnization of the hornfels, it passes into garnet (after plagioclase) and, to a lesser extent, into pyroxene. Moreover, gallium follows aluminum through bimetasomatism, when aluminum is transferred from the "hornfels" into the "limestone" skarns. While following aluminum, gallium enters the crystal structures of garnet and vesuvianite—the most aluminum-rich minerals of "limestone" skarns.

Cobalt and nickel remain very stable in skarnization. As shown in Table 3, there is practically no withdrawal of these elements, especially of cobalt, during skarnization of biotite hornfels. Both nickel and cobalt are in the biotite of the hornfels rocks. On skarnization of the hornfels, they pass into the skarns where they isomorphously replace ferrous iron and manganese. The relatively high content of cobalt and nickel in pyroxenes, in contrast to their concentration in garnets, wollastonites, and vesuvianites* (Table 6) supports our interpretation.

their influx during the skarn-forming process. The migration of the deposit, as indicated by appreciable amounts of tin in pyrrhotites, pyrites, and, especially, sphalerites. Germanium is absent in the sulfides.

Gallium is found in all rocks with the exception of marble, 0.001 to 0.005% on the average, with local "highs" up to 0.01%. Its distribution among skarn minerals is as follows: 0.003% in biotite; 0.005%

Table 6

Mineral	% Co	% Ni
Biotite	0.004	0.01
Plagioclase	-	-
Pyroxene	0.004	0.003
Garnet	-	0.001
Wollastonite	-	-
Vesuvianite	<0.001	0.006
Pyrrhotite	0.005	0.003
Pyrite	0.007	0.003
Chalcopyrite	0.006	0.001
Sphalerite	0.01	0.001

*However, we should note that the Ni content in vesuvianite is very high (Table 6) [Editor].

The cobalt and nickel "highs" in sulfides indicate their possible secessions during the late sulfide stage of formation of the deposit.

Chromium and vanadium. An intensive withdrawal of both these elements is characteristic for hornfels skarns. In biotite hornfels, chromium and vanadium accumulate in biotite. In skarns, vanadium chiefly in pyroxene, garnet, and vesuvianite, whereas small amounts of chromium are distributed uniformly among all skarn minerals (Table 7). Both vanadium and chromium are absent in sulfides.

The association of vanadium with pyroxene, garnet, and vesuvianite appears to sustain the conclusions of some earlier investigators [2, 4], regarding the possible isomorphous replacement of aluminum, ferric iron, and perhaps magnesium by vanadium [5]. In contrast with vanadium, chromium shows no definite preference for any mineral. Therefore, it is not possible to offer any suggestion, however generalized, regarding mechanism of ingress of chromium to crystal structures of skarn minerals.

Titanium, in biotite hornfels, is in rutile and is also fixed in biotite and feldspars. Sphene is formed by skarnization of hornfels, and the bulk of titanium is tied in sphene. Titanium (ionic radius 0.64 Å) follows aluminum (ionic radius 0.57 Å) to some extent and becomes fixed chiefly in aluminum-rich minerals (Table 8). Sphene is a stable mineral in skarn environments; its decomposition is incomplete, and is preserved even in the most severely skarnized rocks. This fact determines the high content of titanium in skarns and the relatively small extent of its isomorphous entry into silicate skarn minerals.

The presence of titanium in sulfide minerals is apparently the result of its partial capture by sulfides during the final sulfide stage of skarn replacement. This is suggested by insignificant amounts of titanium in sulfides (0.001 to 0.005%) together with its relatively high content in skarns (0.2%, and more) (Table 3).

Zirconium is removed most actively during skarnization of biotite hornfels rocks, more so than the other elements (Table 3) where it is originally bound in zircon and, to a lesser extent (0.003%), in biotite. In the resulting skarns, zirconium is associated with garnet (0.03%) and with vesuvianite (0.003%). It is quantitatively absent in all other minerals including sulfides. Kretz and Mitchell [6], in their

Table 7

Mineral	% Cr	% V
Biotite	0.01	0.01
Plagioclase	0.001	-
Pyroxene	0.001 (to 0.003)	0.005
Garnet	0.001	0.003
Wollastonite	0.001	-
Vesuvianite	0.006	0.01

Table 8

Mineral	% Ti
Biotite	up to 1%
Plagioclase	0.16
Pyroxene	0.01
Garnet	0.15
Wollastonite	0.003
Vesuvianite	0.5

studies of the Skaergaard intrusion, concluded that there is a possibility of zirconium-calcium isomorphism in pyroxenes. In our case, however, there is no zirconium whatsoever in pyroxenes, but there are zirconium "highs" in vesuvianites and garnets (up to hundredths of one per cent in some individual cases).

We may suggest, therefore, possible zirconium-calcium isomorphism for garnet and vesuvianite also. Moreover, with a measure of caution, we may suggest that zirconium may prefer the crystal structures of garnet to those of pyroxene in rocks where both these minerals are present, as for example, in pyroxene-garnet skarns.

Strontium and barium are relatively high in biotite hornfels from which they are effectively transferred into marble during skarnization of the hornfels.

The direct association of strontium with calcium silicates is indicated by its distribution in skarn minerals (Table 9) and by its absence in biotite. Barium, on the contrary, accumulates chiefly in biotite, and there is practically no transfer of barium to skarn minerals.

The large ionic radii of strontium and barium (1.27 and 1.4 Å respectively) limit the isomorphism of these elements to calcium and potassium (with ionic radii of 1.06 and 1.33 Å respectively). The associations of strontium with calcium minerals and of barium with biotite indicates probability of isomorphic replacement of calcium by strontium and of potassium by barium.

The bulk of strontium is in the plagioclases of biotite-pyroxene hornfels. On skarnization of this rock, resulting in the formation of pyroxene, garnet, vesuvianite, and wollastonite, strontium enters these minerals by isomorphous replacement of calcium [7].

Table 9

Mineral	% Sr	% Ba
Biotite	-	0.15
Plagioclase	0.2	0.01
Pyroxene	0.008	-
Garnet	0.005	0.002
Vesuvianite	0.1 to 0.5	-
Wollastonite	0.05	-

Table 10

	Major ore-forming elements						
	Si ⁴⁺	Al ³⁺	Fe ³⁺	Fe ²⁺	Ca ²⁺	Mg ²⁺	K ¹⁺
Rare and dispersed elements replacing the major ore-forming elements	Sn ⁴⁺	Ga ³⁺	Co ²⁺	V ³⁺	Zr ⁴⁺	Co ²⁺	Ba ²⁺
	Ge ⁴⁺	V ³⁺	Ni ²⁺		Sr ²⁺	Ni ²⁺	
	Be ²⁺	Ti ⁴⁺			Ba ²⁺ (?)	V ³⁺ (?)	

In contrast with strontium in biotite hornfels, barium isomorphously replaces chiefly potassium in biotite and, to a lesser extent, the calcium in plagioclase. The restricted barium-calcium isomorphism is the principal reason for the severe impoverishment of skarns with respect to barium, since the isomorphous entry of barium into calcium silicate structures is not characteristic of this element in skarnization of biotite hornfels.

Beryllium. The beryllium content of biotite hornfels and skarns is quite uniform (0.001 to 0.003%). During skarnization of biotite hornfels, where beryllium is chiefly in feldspars (0.005%), beryllium passes into the newly formed skarn minerals and tends to accumulate appreciably in pyroxenes (0.005%). Its content in garnets, vesuvianites, and wollastonites does not exceed 0.001%. Beryllium is quantitatively absent in sulfides and biotites. It appears to enter silicate structures, as $(\text{BeO}_4)^{6-}$ by replacement of the silica tetrahedra, $(\text{SiO}_4)^{4-}$ [3].

It is evident from the foregoing considerations that rare and dispersed elements enter crystal structures chiefly of silicate minerals and isomorphous admixtures. The opinions of different investigators regarding their descriptions of individual elements, regarding possible isomorphous replacements, may therefore be summarized in a general table (Table 10) for the elements here discussed.

CONCLUSIONS

1. Germanium and tin are brought in by solutions during formation of skarns.
2. Gallium, cobalt, nickel, chromium, vanadium, titanium, zirconium, strontium, barium, and beryllium are abstracted from biotite hornfels during skarnization. During formation of skarns, these elements are withdrawn at different rates. Chromium, vanadium, titanium, zirconium, strontium, and barium are withdrawn at a rapid rate; nickel is withdrawn at a slower rate; gallium, cobalt, and beryllium are withdrawn at a barely perceptible rate.
3. Part of the rare and dispersed element content of skarns, with the exception of titanium and zirconium, occurs in sphene and zircon. These elements (exclusive of Ti and Zr) do not form minerals of their own and they enter crystal structures of silicates as isomorphous admixtures.

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EDITORIAL COMMENT

This and a related study (Studenikova and Zolotareva, 1958) indicate marked enrichment of Sn, Mo, Re, and to a lesser extent Ge in the skarns of Tyrny-Auz. Why this group of elements should show such preferential concentrations is an intriguing question. Ringwood (1956) has suggested that the role of the gas phase is important in segregating and concentrating trace elements in a magma. Elements possessing halides with high partial pressures (Sn, Mo, and W, for example) may be removed from silicic magmas by distillation into gas bubbles in the mechanism proposed by Fenner (1933). This argument makes sense from both the standpoint of trace element concentrations and mineralogy of the Tyrny-Auz. The remarkable enrichment of Sn in vesuvianite (Table 5) is in harmony with the observation that vesuvianite forms because of magmatically derived fluorine (Turner and Verhoogen, 1951). The common chalcophile elements do not appear to be affected by the distillation mechanism mentioned above, but instead form sulfides which may selectively attach to rising gas bubbles. Perhaps the hydrothermal "extension" of these magmatic processes may apply to skarn formation.

Sn (as well as Be) enrichment in skarns has also been spectrographically documented by Hellwege (1956) in axinite, vesuvianite, andradite, and epidote. Regarding Ge, in view of Mullers and Brasseur's (1956) synthesis of a mica-like mineral in which Si is replaced by Ge, it is interesting to note that in this report there is no enrichment of Ge in biotite; garnet is the scavenger (Table 5).

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THE ORIGIN OF SCHEELITE IN SKARN
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Abstract

Some general geological and mineralogical features of scheelite skarn type deposits are considered. A suggestion has been made of the possibility of the tungsten transfer in skarn ore process with alkaline (essentially sodium) solutions. The scheelite deposition is considered to be the result of exchange reaction $\text{Na}^+ \rightleftharpoons \text{Ca}^{2+}$ between the hydrothermal solution and surroundings. Some experiments are described on modelling the process of the tungsten transfer and scheelite deposition at the interaction of alkaline solutions containing tungsten with some minerals; the experiments were carried out at temperatures 350-400°C and pressures of 250-600 atm.

The available body of geological data and the general theoretical considerations of the mechanisms and forms involved in the transfers of ore-forming elements by hydrothermal solutions or by pneumatolytic emanations allow us to maintain at this time that the formation of scheelite in nature is due to a reaction between tungsten-bearing aqueous solutions or gaseous emanations and the environment in which tungsten is present. There is no single and generally accepted opinion regarding the chemical nature and the phase state of the ore-bearing solutions or regarding the form of the tungsten contained therein. It is commonly believed that tungsten is transferred in the form of its volatile compounds with chlorine or fluorine (i.e. as a halide). This implies an acid gaseous character for the tungsten-bearing fractions. The widespread acceptance of this view appears to depend, to a large extent, on the fact that tungsten deposits associated with greisens and pegmatites, definitely the effects of acid gaseous emanations, fluorine-rich solutions, were drawn into the orbit of industrial and economic importance much earlier than scheelite deposits of the skarn type. And these latter deposits, as a rule, show neither any quantitative correlation between tungsten and fluorine (not to speak of chlorine) nor any time-relationship between the deposition of scheelite and fluorine, according to the literature [1]. This circumstance has led to the development of other viewpoints regarding the possible forms of tungsten transfer of tungsten, for example, as heteropolysilicates [1] or as water-soluble alkali tungstates [2].

It appears that there is but little sense in any excessive specificity in posing the problem of the forms of the transfers of tungsten, as a whole, in view of the extreme complexity of the composition of the ore-bearing fractions themselves and of the practically certain variety of the mechanisms involved in the transfers of tungsten, as determined by variations in the geologic environments, as well as by variations in the forms of tungsten in aqueous solutions or in gaseous emanations, as dependent on time. It appears reasonable, therefore, experimentally to ascertain the general chemical characteristics of a hypothetical hydrothermal tungsten solution in the period directly before the deposition of the ore, in the characteristically skarn-forming environments. The present article discusses some of the experiments along these lines at the Laboratory of Magmatogenic Processes under the direction of N. I. Khitarov.

The experiments were based on certain general features, genetic and geologic-mineralogic, shown by the vast majority of scheelite skarns. These features were made clear by the analysis of a large body of literature on the deposits of this type, as well as by the author's personal studies at the Tyrny-Auz deposit (northern Caucasus). Let us enumerate now the most important characteristics of such deposits, from the point of view of the present study.

1. Scheelite is formed later than the principal ore-forming minerals, pyroxene and garnet, and is superimposed on these minerals. The bulk of scheelite in such deposits is associated with the formations cutting through the skarns (quartz, quartz-silicate, and quartz-sulfide veinlets).

2. Scheelite is the only hypogenic mineral of tungsten in the vast majority of skarn deposits. Wolframite is very rarely found in skarns.

3. As a rule, scheelite is distributed very irregularly in skarns. On one hand, this is due to the association of an appreciable bulk of scheelite with formations cutting across the skarns, as was already stated. On the other hand, this irregularity is due to certain chemical-mineralogic features of skarns of different types. It is significant that scheelite skarns are generally rich in plagioclase of the acid variety (albite, oligoclase). Scheelite is associated with accumulations of plagioclase in many instances; in some instances, scheelite is collected in albitized parts of granodiorite, near its contact with skarnized limestone. Plagioclase is not uncommonly an essential component of the scheelite-bearing quartz-sulfide formations cutting the skarns [3].

4. In most of the skarn deposits of tungsten the deposition of scheelite is accompanied by such processes as the deposition of quartz, albitization of plagioclase (or formation of albite), uralitization of pyroxene, i.e. processes that take place chiefly in alkaline environments.

Many of the characteristics here listed belong also to the Tyrny-Auz deposit. However, basic plagioclase (andesine-labradorite) is

veloped conspicuously in the Tyrny-Auz skarns. The largest accumulations of scheelite are found there especially in pyroxene-plagioclase skarns, with the plagioclase of An_{50-60} , formed at the expense of pyroxene hornfels whose plagioclase is An_{70-80} . The pyroxene-plagioclase skarns contain accordingly more Na_2O than is found in any other variety of the Tyrny-Auz skarns. All of this leads us to the supposition that the tungsten-bearing hydrothermal solutions were alkaline (essentially sodium), at least at the time of the deposition of scheelite in the skarns. The deposition of scheelite may be regarded as a cation exchange between Na^+ of the mineralizing solution and Ca^{++} of the silicates of the host rock (skarn). Moreover, the completeness of the deposition of wolframite would depend on the extent of fixation of Na^+ in the solid alumino-silicate phase of the skarns, inasmuch as the presence of Na^+ in the solution would interfere with the complete precipitation of tungstate by calcium. It is for this reason that the plagioclase-rock varieties of skarns constitute the most favorable environments for the precipitation of tungsten. Indeed the cation exchange reaction, $2Na^+ \rightleftharpoons Ca^{++}$, would be favored especially by interactions between plagioclase and the alkaline tungsten-bearing solution resulting in the albitization of plagioclase and in the deposition of scheelite. The newly formed albite would be also conducive to the same result, i.e. to the fixation of Na^+ by the solid phase. When the same solution reacts with other ordinary skarn silicates, however, (pyroxene and garnet), the $2Na^+ \rightleftharpoons Ca^{++}$ exchange appears to lose its prominence to other processes which result in a liberation of calcium, such as the amphibolitization of pyroxene or the replacement of the silicates by quartz. In this latter case the deposition of scheelite will depend quantitatively on the stability of the corresponding silicate in the alkaline solution.

It appeared feasible to test these suppositions about the chemistry of tungsten solutions and regarding the mechanism of the precipitation of scheelite by appropriate model experiments. The experiments were conducted in the N. I. Khitarov diffusion apparatus shown schematically in Figure 1. The flow reactor in the muffle was charged with 1 to 1 cm fragments of the desired mineral. The temperature and pressure in the system were maintained automatically and independently from each other at a pre-determined level. The rate of flow of the solution in the reactor was maintained at 40 to 50 mph, on average. At the end of the experiment the charge of the reactor was examined for $CaWO_4$.

This study was conducted with the aid of the short-wave ultraviolet radiation of the samples under which $CaWO_4$ shows a brilliant blue fluorescence. Some of the samples were analyzed for their structure by the X-ray method, to ascertain identity of the synthetic products with natural scheelite. We are indebted to E. S. Makarov for this assistance. Wherever the luminescent synthetic product was present, the diffraction pattern of the sample showed every one of the scheelite

We confined the future identifications to the ultraviolet method

Table 1. Data on X-ray Diffraction Patterns of Synthetic CaWO_4 .
Copper radiation; nickel filter; diameter of chamber 57.3 mm;
diameter of sample 0.6 mm

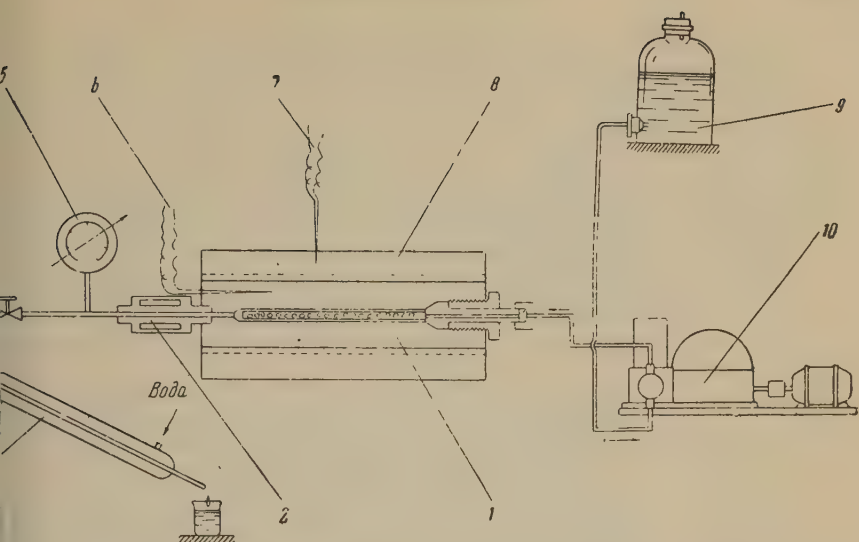
Item	Intensity, I	Synthetic CaWO_4	Natural scheelite	Item	Intensity	Synthetic CaWO_4	Natural scheelite
1	3	4.763	4.76	20	6	1.432	-
2	3	3.528	-	21	6	1.417	-
3	2	3.371	-	22	4	1.352	-
4	3	3.116	3.09	23	4	1.335	-
5	10	3.053		24	4	1.294	-
6	2	2.844	2.83	25	4	1.245	1.243
7	1	2.617	2.61	26	4	1.234	-
8	6	2.504	2.49	27	2	1.210	1.200
9	2	2.413	-	28	3	1.178	1.165
10	8	2.283	2.28	29	4	1.153	-
11	8	2.100	1.98	30	3	1.139	-
12	9	1.907	1.92	31	1	1.122	-
13	9	1.863	1.85	32	2	1.081	1.080
14	2	1.684	1.67	33	2	1.059	-
15	3	1.618	1.62	34	7	1.048	-
16	5	1.597	1.58	35	4	1.033	-
17	3	1.548	1.54	36	6	1.008	1.010
18	4	1.512	-	37	2	0.9807	-
19	2	1.465	-				

accordingly. The readings of one diffraction pattern are reported in Table 1, together with the published data [4] on the structure of natural scheelite.

The first series of experiments was carried out in order to verify the possibility of formation of scheelite by the reaction between an alkaline solution containing tungsten and calcium aluminosilicates that are common in skarns. Taking into account the previously stated proposition, namely, that the richest scheelite mineralization is associated with the plagioclase-rich zones of the skarns, we used a basic plagioclase (labradorite) in the experiments. The samples were previously tested in ultraviolet light, to make sure that they contained no luminescent materials. The experimental conditions and the results are stated in Table 2.

The first two experiments with the solution of Na_2WO_4 resulted in the formation of CaWO_4 , as a rim on the fragments of plagioclase. This formation was more intensive at 500°C and 600 atmospheric pressure than at the lower parameters (350°C and 250 atm.), despite the weaker concentration of the solution and the shorter duration of the experiment.

In the next two experiments (Nos. 3 and 4), in which more complex and more alkaline solutions were used, there was no formation of CaWO_4 whatsoever. The mineral neotypes were represented instead by small and well formed crystals of analcime and possibly of natrolite distributed more or less uniformly over the strongly bleached



1. Plan of the Khitarov Diffusion Apparatus: 1—Reactor and charge; 2—condenser; 3—valve; 4—manometer; 5—thermocouple and millivoltmeter; 6—thermocouple to rheostat; 7—resistance muffle; 8—solution; 9—pump, pressure.

face of the plagioclase fragments. The formation of scheelite may take its place apparently only in relatively weakly alkaline media. The second series of experiments was intended to serve as a model for the transfers of tungsten in alkaline solutions, as a whole, and for the deposition of CaWO_4 in alkaline environments, while demonstrating the instability of wolframite and the consequent impossibility of its formation under such conditions. This series of experiments was performed in the same diffusion reactor. The minerals were placed in

Table 2. Experiments with Interactions between Alkaline Tungsten Solutions and Labradorite

Solution	Charge	Temp., °C	Pressure, atm.	Duration, hrs.	Result
0.05N Na_2WO_4	labradorite	350	250	17	CaWO_4 in isolated spots on the surface of labradorite
0.02N Na_2WO_4	"	500	600	10	CaWO_4 as unbroken crust on labradorite
0.015N Na_2WO_4 0.2N NaOH; 5g. SiO_2 per liter	"	350	250	10	No CaWO_4 ; analcime formed
0.05N Na_2WO_4 0.15N NaOH; 5g. SiO_2 per liter	"	350	250	8	No CaWO_4 ; analcime formed

Table 3. Experiments with Transfers of Wolframite and Deposition of Scheelite in Some Alkaline Solutions

Expt. no.	Solution	Charge	Temp., °C	Pres. atm.	Contact hours	Results
1	0.005N NaOH	Wolframite (with quartz) labradorite and limestone	350	250	14	Wolframite decomposed; CaWO_4 deposited, chiefly on limestone
2	0.025N NaHCO_3	Wolframite (with quartz) and labradorite	500	600	5	Wolframite decomposed; CaWO_4 deposited
3	H_2O	Albite, wolframite, and limestone	500	600	4	Wolframite slightly decomposed; a small amount of CaWO_4 deposited

the reactor in the sequence shown in Table 3 with respect to the path of the circulating solution. Thus, for example, in Experiment No. 1, wolframite and quartz were placed at the inlet of the autoclave; labradorite was next; limestone was placed at the outlet of the autoclave.

The first two experiments serve as clear evidence of the possibility of the transfers of tungsten in weakly alkaline solutions and of the possibility of the deposition of scheelite in the same weakly alkaline environment in the presence of calcium. They show also that wolframite is unstable and cannot possibly be deposited in such environments. Under the experimental conditions, the wolframite, while undergoing decomposition, was becoming coated by a brown crust, consisting of iron and manganese hydroxides, and the CaWO_4 was settling on the surface of either labradorite or limestone, chiefly at the outlet of the reactor.

In Experiment No. 3 (Table 3), the transfer of wolframite was made effective by a complicated solution resulting from the reactions between water and albite at high temperature and pressure. This solution resembled apparently the solution resulting from reactions between water and oligoclase, under the same conditions. According to N. I. Khitarov [5], this latter solution contains 53 mg/l SiO_2 , 18 mg/l Al_2O_3 , and 7.0 mg/l Na_2O at 500°C and 600 atm. In the experiment here described, in the presence of limestone in the reactor, the solution was complicated further by the presence of HCO_3^- and CO_2 , to the point that it could be seen as a simplified model of a natural hydrothermal solution carrying tungsten, on the first approximation.

Some of the chemical-mineralogic alterations in skarns, in the e-proximity of the deposition of scheelite, may be explained also the alkalinity of the mineralizing solutions. Preliminary experiments with stability of pyroxene (diopside-hedenbergite) and garnet (andradite-grossularite) in alkaline solutions (Table 4) indicate a relatively high stability of garnet in such environments. The principal constituent dissolved out of the pyroxene is SiO_2 . We cannot exclude possibility of the replacement of pyroxene by garnet plus quartz which is a more stable combination, in the alkaline environment in question. The oxidation of iron, Fe^{2+} to Fe^{3+} , a prerequisite for the replacement, may take its place easily also in the alkaline environment.

Table 4. Experiments with Stability of Pyroxene (Diopside-Hedenbergite) and Garnet (Andradite-Grossularite) in Alkaline Solutions (0.15N NaOH*)

Mineral	Temp. °C	Pressure, atm.	Sample no.	Duration of sampling, hrs.	Mg per liter		
					SiO_2	Al_2O_3	CaO
Pyroxene	350	250	1 to 5	5	3362	34	2.37
"	"	"	6 to 10	5	3636	30	3.16
Garnet	350	250	1 to 5	5	209	33	0.79
"	"	"	6 to 10	5	270	34	1.97

I. Shekhanova, Analyst.

As a whole, the experimental results confirm the supposition regarding the transfer of tungsten and the deposition of scheelite in highly alkaline solutions. The results are also in harmony with the relationships observed in nature and with certain other experimental findings pertinent to the problem in question. From our point of view it becomes quite simple to explain such phenomena as the association of high-grade scheelite ores with plagioclase-rich parts of skarns, the common absence of wolframite in skarn deposits of scheelite, and the invariable silicification (quartz) of mineralized skarns. Thus Mel's experiments with albitization [6] show that the excess of silica becomes crystallized as quartz only in alkaline but not in acid solutions.

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HAFNIUM - ZIRCONIUM RATIOS IN METAMORPHIC
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Abstract

The distribution of zirconium and hafnium in 14 rock samples from the Upper of the Krivoi Rog series has been studied. It has been shown that the zirconium oxide content in unaltered metamorphic rocks varies from 3×10^{-3} to 10^{-3} per cent wt.; the $\frac{\text{ZrO}_2}{\text{HfO}_2}$ ratio varies from 20 to 40. In metasomatic rocks (especially in sodium metasomes) an appreciable enrichment in zirconium is observed (up to 170×10^{-3} per cent wt.). The $\frac{\text{ZrO}_2}{\text{HfO}_2}$ ratio for the same rocks increases sharply up to 112 which is in agreement with the data on zircons obtained by the authors earlier. This phenomenon can be explained by the differences in the migration capability of zirconium and hafnium during sodium metasomatism as hypothetical carbonate complexes and by the different values of their radii and ionization potentials.

The zirconium-hafnium ratio in zircons changes rather abruptly in the presence of zirconium, in metasomatic rocks farthest away from the hypothetical center of the infiltrating solutions, as we showed in an earlier publication [1]. Inasmuch as there is a complete transformation of the rock during the metasomatism due to fundamental changes in the chemical and mineralogical composition of the rock resulting from its complete and repeated recrystallization, it is reasonable to suppose that zirconium and hafnium of such rock should be also subjected to a redistribution. It is highly important, therefore, to ascertain the distribution of zirconium and hafnium both in the original metamorphic rocks and in their metasomatic derivatives. Characteristically, if the dispersed zirconium is observed in an association with micas (in schists), in the least metamorphosed original rocks, it is found in far more irregularly distributed accumulations in the metasomatics.

The analytical procedure consisted of a preliminary up-grading of the sample, by a decomposition of a 10 gram aliquot, and by the subsequent isolation of zirconium together with hafnium. The per cent extraction of zirconium was determined by the added radioactive tracer, Hf^{181} , and was as high as 90 to 95%. The sample was analyzed by the X-ray spectrographic method, as previously described. The results are presented in Table 1.

Table 1. Hafnium and Zirconium in Rocks of Upper Suite
Krivoi Rog Series

Sample no.	Material and source	% by Weight		ZrO ₂ /HfO ₂
		ZrO ₂ x 10 ³	HfO ₂ x 10 ⁴	
<u>Middle Krivoi Rog</u>				
1	Dolomite	7.0	3.5	20
2	Chlorite schist	24.0	6.2	40
3	Carbonaceous limy shale	44.0	11.0	40
4	Carbonaceous pyritized schist	3.60	1.4	25
5	Carbonaceous micro-schist	3.20	1.1	29
Variation		3 to 44	1 to 11	20 to 40
<u>Northern Krovoi Rog</u>				
6	Magnetite-amphibole quartzite	21.0	6.7	31
7	Aegirinite	11.0	2.5	40
8	Magnetite	< 1.0	-	-
9	Mica-garnet schist	15.9	3.47	48
10	Mica schist	8.8	2.65	33
11	Weakly albitized schist	25.6	8.74	31
12	Albitite	72.6	23.0	33
13	Albitized carbonaceous schist	102.0	13.6	75
14	Amphibolitized ferruginous quartzite	170.0	1.5	112

The first five samples are the most typical rocks of the Upper Suite, the Krivoi Rog Series, at some distance from any area of their metasomatic alteration. They represent, accordingly, the average composition of the Upper Suite of the metamorphic units of the Krivoi Rog.

Characteristically, our results are very close to the averages of zirconium in acid igneous rocks ($2 \times 10^{-2}\%$) and the typical ZrO₂/HfO₂ ratio (30 to 40), as previously established by L. Ahrens.

The second series of our samples is represented by both metamorphic and metasomatic rocks of the Northern Krivoi Rog. This series is characterized by a considerable variation in the content of zirconium and hafnium, indicative of a truly fundamental re-sorting of the chemical substance by the metasomatic process. Petrographic studies show that either magnetite-amphibole iron ore deposits or aegirinites may be the result of metasomatic alterations of quartz-amphibole-magnetite schists. If the rock subjected to such alterations is high in alumina, such as the quartz-biotite schists, the end-product is either an albitized schist or a practically mono-mineralic albitite.

Samples 6, 7, and 8 (Table 1) show that the formation of magnetite ores, after the quartz-amphibole-magnetite schists, is accompanied by a withdrawal of silica and also of practically all of the zirconium, so that the residual zirconium is decreased to $1 \times 10^{-3}\%$, as against

$\times 10^{-3}\%$ in the original rock, to the point that the determination of the $\text{ZrO}_2/\text{HfO}_2$ ratio becomes no longer feasible.

In contrast with magnetites, the relative constancy of the zirconium-hafnium ratio, as well as the relative stability of their content on the replacement of quartz-magnetite-amphibole schists by aegirinites, in sodium metasomatism (Samples 6, 7) serves once again to emphasize the low degree of probability of the formation of aegirinites directly after magnetites, inasmuch as, were it so, it would be impossible to explain the sudden increase of the content of Zr and Hf. Indeed, the entire series of petrographic-mineralogic observations shows consistently that the presence of silica, as quartz, is indispensable in argillaceous rocks undergoing aegirinitization.

Thus the withdrawal of silica during the formation of magnetite takes place concurrently with the withdrawal of zirconium and constitutes an irreversible geologic process.

The replacement of mica schists by albitite (Samples 9, 12) is a clearly diagnostic phenomenon, petrographically, both in the field and in the laboratory; it is conducive to a noticeable enrichment of the rock in zirconium and to its parallel enrichment in hafnium. The $\text{ZrO}_2/\text{HfO}_2$ ratio remains constant even with a five-fold increase in the zirconium content of albitite, as against the mica schist.

It is curious, in this connection, that some individual large accumulations of zircon in these rocks [1] are characterized by a definitely high $\text{ZrO}_2/\text{HfO}_2$ ratio. Consequently, the previously noted hafnium lag finds its expression only in places of the highest zirconium enrichment, due to the irregular rates of the metasomatic processes. Our last two samples (13 and 14), taken from rocks at some distance from zone of the metasomatic peak, but subjected nevertheless either to some insignificant albitization and to an enrichment in sphene (Sample 13) or distinguished by the presence of secondary amphibole (Sample 14), serve to illustrate this pattern.

In such manner, there is no doubt whatsoever as to the difference between the migration capacities of hafnium and zirconium in solutions containing sodium together apparently with carbonic acid, in the course of the endogenic formation of minerals. What are the structural features, then, of hafnium and zirconium atoms and of their compounds that would help us account for the effects here described?

Table 2. Some Characteristics of Zirconium and Hafnium

Element	Ionic radius Å	Ionization potential according to J. Green, 1953	Heat of formation of oxides, according to D. Kay and T. Levy, 1955
Zirconium	0.82	31.0	258.1
Hafnium	0.78	33.83	271.5

A partial answer to this question is given by a comparison of some chemical properties of the two elements in Table 2. The comparison shows that the slightly larger ionic radius of zirconium, with the same valence of both, has its expression in the somewhat lower stability of the compounds of this element, as against stability of analogous compounds of hafnium. Zirconium ions pass into solution also somewhat more readily than hafnium ions, judging by the ionization potentials.

Consequently, differences in the behavior of these two elements are quite appreciable, on the geologic time-scale, despite the insignificant differences in their chemical properties. One may draw a general conclusion, it appears, that parting of couples of elements closely resembling each other is the more conspicuous, the longer the natural geologic process responsible for their parting, all other factors being the same.

The same effect should be manifest also in the migrations of titanium, whose properties differ from those of hafnium even more than the properties of zirconium. The appreciable enrichment of schists in sphene (Sample 13, Table 1) indicates that titanium was migrating to a greater extent than zirconium, in the given environment—a subject of considerable interest in this connection.

One must have in mind that our conclusions regarding the mechanisms of transfers of the elements would be unduly restricted, were we to think only in terms of their ions. In practice, migrations of these elements in natural environments depend on the existence of their soluble and stable complexes, as was shown in the provisional text of our report "On Relationships in the Distribution of Rare Earths, Zirconium, and Hafnium in Igneous Rocks" [2].

Thus the carbonate alkali complexes of this type, in the instance of the rare earths, serve truly to explain the relatively rapid selective precipitation of the cerium earths, whereas the yttrium earths are retained in solution for an appreciably longer time. Were we to assume that the rare earths are present in the solution as simple ions, the sequence of their separation based on the solubility of their phosphates would be the very opposite of the known sequence, as was remarked correctly by E. Ingerson.

Both effects are operative in the same direction, in the case of zirconium and hafnium. In other words, zirconium passes into solution before hafnium both at the time of the solution of the rock and at the time of the redeposition of zircon.

The presence of any one of the previously listed complexes in the solution [1] also will be conducive to a noticeable lagging of hafnium, in comparison with zirconium, during their subsequent migration.

Consequently, indicator elements of the type of the couple here studied enable us not only to appraise the chemistry of the reaction here involved but also to appraise the span of their duration, as expressed by the extent of parting of these two elements.

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PROPORTIONS OF RARE EARTHS IN GADOLINITES

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Abstract

X-ray structural and X-ray spectral studies of 5 samples of gadolinite from pegmatites of Sweden, Norway and the Caucasus have been carried out. The results show that the ratio of cerium earths is relatively constant whereas the ratios of yttrium earths show slight variations. These variations do not influence the structure of the minerals. The existence of cerogadolinite is hardly possible.

Among the seven types of rare-earth minerals, a type of the so-called average composition was recognized by K. Rankama and T. Sahama in 1950 [3]. This type is identified by the presence of about the same proportions of the rare-earth metals within both the yttrium and the cerium groups ($\text{Ce} = \text{Nd}$) and often also by $\text{Nd} - \text{Sm} - \text{Gd}$. We investigated a gadolinite, one of the minerals of such type, and found indeed that it contains the characteristic proportions of the rare earths.

E. I. Semenov [4] classifies gadolinite with the minerals of so-called complex composition, i.e. with the minerals distinguished by eight-fold coordination of their rare earths and, according to this author, also by their high capacity for isomorphous substitutions. In other words, like allanite and pyrochlore, gadolinite may contain the rare earths with a highly variable $\Sigma \text{Y} / \Sigma \text{Ce}$ ratio.

Indeed, there are indications in the literature [1] regarding existence of "cerogadolinite" (up to 23.4% Ce_2O_3) and calcium gadolinite (11.91% CaO), although none of these reports was confirmed by X-ray analysis of the mineral structures.

The common "yttrium" surroundings of gadolinite in pegmatites are expressed by the characteristic paragenesis of the minerals: zircon, garnet, yttrio-allanite, yttrialite, fergusonite, which makes us doubt, naturally, the existence of cerium varieties of gadolinite, inasmuch as the composition of gadolinite, as a complex mineral, must reflect the proportions of the rare earths in the mineral's environment.

At the same time, gadolinite may prove to be a sensitive indicator of the geochemical environment in which it is formed, as we are led to believe, due to its belonging to the rare-earth minerals of complex composition. With this purpose in mind, we investigated specimens of gadolinite from Sweden, Norway, and the USSR. The results of the X-ray spectrographic and the X-ray structural analyses are presented in Tables 1 and 2.

Table 1. Proportions* of Rare Earth Elements in Gadolinites

Proportions†	1. Ytterby, no. 51372 Sweden	2. Ytterby no. 3 Sweden	3. Falun no. 51374 Sweden	4. Hittero no. 51366 Norway	5. Indysh River N. Caucasus (G. D. Afanasev's specimen)
La/Nd	-	-	-	-	-
Ce/Nd	0.50	0.67	0.53	0.73	0.6
Pr/Nd	0.19	-	0.19	0.21	0.17
Sm/Nd	0.65	0.85	0.74	0.68	0.69
Gd/Nd	0.83	1.0	0.96	0.85	0.81
Tb/Nd	0.22	0.33	0.29	0.195	0.20
Dy/Nd	1.1	1.7	1.65	1.25	1.15
Ho/Nd	0.27	0.48	0.35	0.35	0.22
Er/Nd	0.62	1.2	1.0	0.82	0.83
Tu/Nd	-	-	-	-	0.11
Yb/Nd	0.5	1.5	0.73	0.84	1.0
Lu/Nd	0.11	0.31	0.13	0.185	0.22
J/Nd‡	10	15	12.3	9.2	12

In the original "raspredelenie", "distribution". VPS

In the original "otnositel'noe soderzhanie elementov", "the relative content of the elements". (It is evident from the context that the foregoing elucidations are not only justified but are almost obligatory.) VPS

"J" is the Rus. for "I", iodine. This is not explained in the text. All of the 14 rare earths are accounted for in the Table. Could "J" be a misprint for "Y", yttrium? VPS

These results indicate relative constancies in the proportions of cerium rare earths in our minerals, together with insignificant variations in the proportions of the yttrium rare earths, with the total rare-earth content of about 40%. These variations in the composition have no effect whatsoever on the mineral structures, inasmuch as the X-ray patterns were fully identical for all of the minerals examined. The absence of some minor lines in the X-ray patterns of the Hitterö No. 51366 and of the Ytterby No. 3 is merely a sign of a partial decomposition of the lattice structures, very much as happens in allanite in the presence of some radioactive constituents.

Characteristically, the greatest difference in the proportions of the cerium earths (1.5 to 2 times; Specimens 1 and 2, Table 1) was observed in gadolinites from one and the same deposit of Ytterby, Sweden.

Our results sustain the classification of gadolinite with the rare-earth minerals of complex composition as well as the probability of variations in the amounts of the yttrium earths in gadolinite due to their relatively high mobility in the pegmatitic melt, as against the immobile cerium earths [2].

Despite constancy of the parameters in the structures of gadolinite and of the gadolinite paragenesis with the yttrium minerals, we still are in doubt regarding the possibility of the existence of cerogadolinite.

Table 2. Gadolinite, Interplanar Distances
(Fe K α B, 35 Kv., 12 m.a., 2R = 57.3mm)

Ytterby, no. 513721		Hitterö, no. 51366		Indysh River		Ytterby no. 3	
d/n	I	d/n	I	d/n	I	d/n	I
4.73	6	4.73	6	4.73	7	4.73	6
-	-	4.14	2	3.66	1	-	-
3.51	8	-	-	3.51	2	-	-
3.43	5	3.44	5	3.41	3	3.44	5
8.23	1	-	-	-	-	-	-
3.11	10	3.10	10	3.12	10	3.11	9
3.03	2	3.03	2	-	-	-	-
2.93	5	2.93	5	2.94	3	2.94	5
2.81	10	2.81	10	2.83	10	2.81	10
-	-	-	-	-	-	2.70	2
2.55	9	2.55	8	2.56	8	2.56	9
-	-	-	-	2.46	1	2.42	2
2.36	5	2.35	5	2.37	4	2.35	5
2.24	2	2.22	4	2.24	2	-	-
2.20	5	-	-	2.20	5	2.20	6
2.16	1	-	-	2.13	1	-	-
2.05	2	-	-	2.04	3	-	-
2.02	2	2.01	2	-	-	-	-
1.964	7	1.958	6	1.964	6	1.958	4
1.861	8	1.872	8	1.861	7	1.872	6
1.761	7	1.759	7	1.771	6	1.761	5
-	-	-	-	1.707	1	-	-
1.669	2	-	-	1.661	8	-	-
1.653	8	1.653	7	1.633	7	1.657	7
1.626	7	1.622	3	-	-	-	-
1.567	7	1.567	5	1.567	6	1.571	3
1.483	1	1.474	1	1.474	1	1.495	1
1.448	2	-	-	1.442	5	-	-
1.418	3	1.418	5	1.418	4	1.415	3
1.402	3	-	-	1.395	5	-	-
1.318	1	-	-	1.327	3	-	-
1.285	4	1.281	4	1.281	3	1.281	2
1.248	3	1.246	3	1.248	3	1.244	1
1.201	2	1.198	1	1.211	1	-	-
1.180	4	1.185	1	1.295	2	1.180	3
-	-	1.178	2	1.179	4	-	-
1.164	1	1.158	2	1.160	3	-	-
1.145	2	1.147	2	1.140	2	-	-
1.106	6	1.106	2	1.106	2	-	-
1.085	5	1.088	2	1.087	5	-	-
1.071	3	-	-	1.076	1	-	-
-	-	-	-	1.065	1	-	-
1.050	2	-	-	1.054	1	-	-
1.036	4	1.036	1	1.038	2	-	-
1.022	1	-	-	1.017	5	-	-
-	-	-	-	0.991	1	-	-

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AN EXPERIMENT IN BIOGEOCHEMICAL PROSPECTING FOR MOLYBDENUM IN ARMENIA

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Abstract

On the basis of studying the molybdenum distribution in soils and plants of the Kadzharansk ore region (Armenia), it has been shown that copper-molybdenum deposits can be easily discovered from the surface by the analysis of soils and plants. The molybdenum content in the chestnut-coloured soils above the ore zone varies from 1.0×10^{-3} to 3.0×10^{-2} per cent and in the plant ashes from 3.0×10^{-3} to 1.0×10^{-1} per cent, being many times higher than the usual molybdenum content.

There is a certain correlation in molybdenum content between the ore at a depth and the plants (and soils) on the surface. The maps made according to the molybdenum concentrations in the soils and plants exactly outline the dissemination halo of the new ore zone on the left bank of the Okhcha river. The investigations have proved the efficiency of the biogeochemical prospecting for molybdenum in Armenia.

In order to test effectiveness of the biogeochemical method of prospecting for ore deposits in different zones of the USSR, the V. I. Vernadskii Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR, conducted reconnaissance in Southern Ural, in Tuva Autonomous Area, in Eastern Transbaikalia, in Northern Caucasus, and in Trans-Caucasia. The results of these studies were brought to light in the articles by A. P. Vinogradov [1, 1a] and D. P. Malyuga [2, 3, 4, 5, 6].

Biogeochemical investigations were centered in the Armenian SSR, in recent years, chiefly at copper-molybdenum and lead deposits. The present article is a report on molybdenum.

M. N. Senilova made a molybdenum survey in soils and vegetation at the Shalgin deposit as early as 1947. She observed the high mobility of molybdenum in the zone overlying the ore, as expressed by the accumulation of molybdenum in soils and plants. Thus the ash of *Artemisia ferrae albae* had up to 0.01% Mo.

Similar studies were carried out by us in 1952-1954, at the molybdenum sites of Kyzyk-Chadra (Tuva) and in Eastern Transbaikalia (Bugdaya), as well as by V. V. Baranova at the Tyrny-Auz and by V. Marmo [8] at Rauzio, Finland. Let us consider, first of all, the geochemical characteristics of molybdenum.

GEOCHEMICAL CHARACTERISTICS OF MOLYBDENUM IN
THE EARTH'S CRUST

The geochemistry of molybdenum is insufficiently well known both in the abyssal and in the surficial environments of the earth's crust.

E. Fersman [9] has remarked, in his time, that "We are just beginning to understand" the behavior of molybdenum in the supergene environments. The forms in which molybdenum is present in igneous rocks, soils, and sediments remain obscure to this day.

Molybdenum is a typical metallic element of many valences. It is known in its tetravalent and hexavalent states in geochemistry. The first one of these is characteristic for depths, the second one chiefly for surficial environments.

The specific geochemical properties of molybdenum are as follows: 1) Formation of the sulfide, MoS_2 (molybdenite), which is stable at relatively high temperatures. 2) Formation of volatile halides—particularly MoF_6 —by the hexavalent Mo. 3) A high mobility of Mo^{6+} compounds in the surficial environments. 4) An easy incorporation of molybdenum by vegetation.

Table 1 cites the average concentrations of molybdenum in igneous rocks, according to A. P. Vinogradov [10], together with the concentrations of molybdenum in natural waters, soils, and vegetation.

The data in Table 1 do not suggest any strictly defined tendency of molybdenum to be associated with any definite type of rocks. Molybdenum becomes distributed uniformly among all members of the magmatic series, in the course of magmatic differentiation. The presence of molybdenum in the alkali and the plagioclase feldspars of certain granites and the silica-molybdenum relationship suggest, nevertheless, that molybdenum is connected with the later rock series (granites and granitoids).

Table 1. Relative Abundance of Molybdenum in the Earth's Crust

Materials	% Mo	Authority
Crustal Lithosphere	2×10^{-4}	A.P. Vinogradov [10]
Granitic rocks	4×10^{-9}	"
Basaltic rocks	1.4×10^{-4}	"
Intermediate rocks	9×10^{-5}	"
Sedimentary rocks	1.9×10^{-4}	"
Sedimentary rocks	2.0×10^{-4}	"
Natural surface waters	1.0×10^{-7}	P.K. Kuroda et al. [11]
Soils, average	2.0×10^{-4}	A.P. Vinogradov [12, 13]
Humus-podzol soils	2.0×10^{-4}	Kh. G. Vinogradova [14]
Chernozem soils	2.0×10^{-4}	"
Forest soils	2.5×10^{-4}	"
Volcanic ash	1.0×10^{-3}	"

Table 2. Molybdenum Content of Minerals in Biotite Granites, Tyrny-Auz

Mineral	% of mineral in rock	Mo in mineral, micrograms per gram	% of total Mo in rock represented by mineral
Quartz	28.9	0.01	0.3
Feldspars	62.4	1.20	79.0
Biotite	8.1	2.30	19.6
Accessory minerals	0.06	13.20	1.1

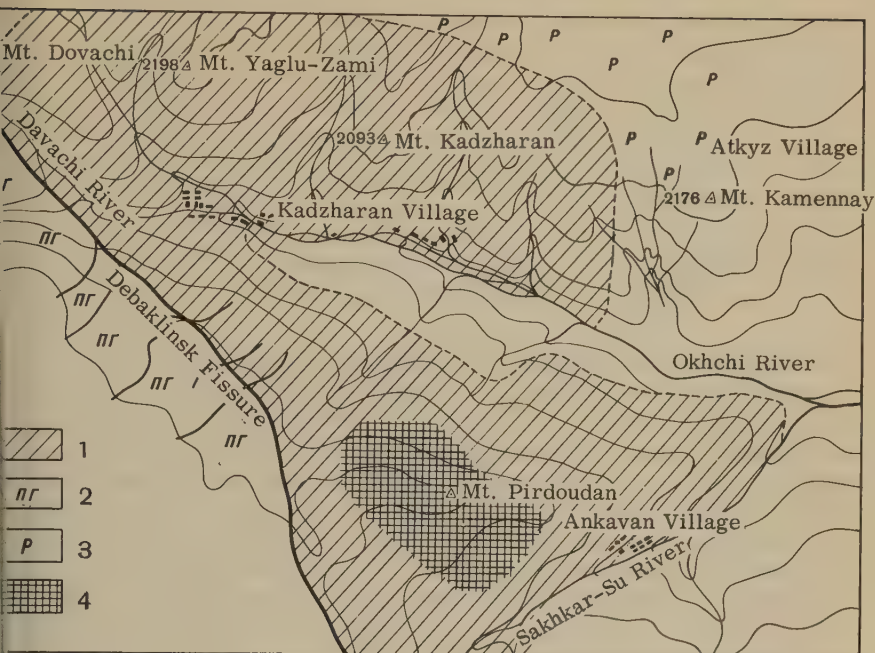
The distribution of molybdenum in rock-forming minerals may be illustrated by data on the biotite granites of El'dzurtin (Tyrny-Auz, N. Caucasus) investigated by Z. V. Studenikova, M. I. Glinkina, and L. I. Pavlenko [15] (Table 2). One may see in Table 2 that 4/5 of the total molybdenum of the granite may be explained by replacement of Fe^{3+} (ionic radius 0.67 Å) and Ti^{4+} (ionic radius 0.68 Å, according to Ahrens) by Mo^{4+} (ionic radius 0.68 Å). We cannot exclude the possibility of the entry of molybdenum into crystal structures of magnesium silicates and aluminosilicates by replacements of aluminum and magnesium by Mo^{4+} . Let us consider now certain field data on testing the usefulness of the biogeochemical prospecting in reconnaissance at the copper-molybdenum deposit of Kadzharan (Arm. SSR).

GENERAL GEOLOGIC INFORMATION ON THE DISTRICT

The Kadzharan District is a typical high-mountain terrain more than 2000 meters above sea level, severely dissected by large and small surface streams (the Okhchi, the Sagkar Rivers, and others). The relief is typical of the geologically young high-mountains of southeastern Armenia.

Tertiary intrusives: porphyrites, porphyry granites, and monzonites take part in the structures of the district. The copper-molybdenum ores of Mt. Pirdoudan are associated with monzonites bordering on porphyry-type granites in the southwest, along the Debaklin Fissure, and on the contact hornfels in the north (Fig. 1).

The Recent sediments consist of alluvium and diluvium. They are not very well developed in the Kadzharan because of the steepness of the slopes. Alluvial and diluvial sediments attain their maximum thickness on the northern slopes of Mt. Pirdoudan, in the trough facing the steep bank of the Okhchi River near the Kadzharan Village, where the total thickness of Recent sandy-clayey and rubbly sediments is up to 10 to 20 meters. Most of the terrain (up to 80%) is mantled by a relatively thin soil and diluvium, 1 to 5 meters thick. However, weathering of the ore-bearing rocks is traceable to appreciable depths



1. Geologic pattern of the district: 1—monzonites; 2—porphyro-granites; 3—hornfels; 4—the ore zone.

throughout the District. Effects of weathering are noticeable in the faults and fissures in the host rocks, especially where these are particularly accessible to the action of natural solutions, and are more thoroughly hydrated accordingly.

The monzonites of which the mineralized zones are composed, in Kadzharan, were altered severely by hydrothermal processes. Monzonites, as a whole, range from dark gray medium-grained fresh rock to weakly altered rock, kaolinized along fractures. The mineralized monzonites are grayish white or brown, commonly ferruginous, silicified (quartz), and kaolinized; they are riddled by quartz and sulfide veins in their ore zone.

Diluvium of clayey materials and, more rarely, of sandy materials, "vesva"* (rubble), and large fragments of igneous rocks. Diluvium over the bedrock is strongly kaolinized. The surface of the diluvium is mantled by a fairly stable layer of soil.

Kadzharan is but a small part of a large metallogenic province extending southeastward from the northwest of Armenia. This province contains several polymetallic, copper-molybdenum, and

*"vesva", in sedimentology, is an eluvial product of weathering rocks, usually granite, consisting of unrolled grains of the rock or minerals. VPS

copper ore deposits: Kafa, Agarak, Dzhindar, Bugakar, although, as a whole, the province is still insufficiently well known, according to S. S. Mkrtchyan [16].

Applications of the integrated geochemical investigations will lead to a more rational organization of exploration and mining work, particularly in the newly discovered promising areas of Kadzharan, Agarak, Dastakert, and others.

MINERALOGY AND CHEMISTRY OF PROCESSES IN THE OXIDIZED ZONE OF A COPPER-MOLYBDENUM DEPOSIT

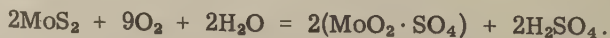
The hydrothermal copper-molybdenum mineralization in the Kadzharan is characterized by the following paragenesis of the primary sulfide minerals: chalcopyrite, CuFeS_2 ; molybdenite, MoS_2 ; pyrite, FeS_2 ; galena, PbS ; sphalerite, ZnS ; argentite, Ag_2S ; "dull ores," $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (the tetrahedrite group). The ore minerals are in quartz veins and veinlets and are also dispersed in the host rocks (both the vein-network and the disseminated type of mineralization), according to I. G. Magakyan [17] and N. A. Akopyan [18].

There are appreciable amounts of tungsten, vanadium, and rhenium that are in places found together with molybdenum. There are other specific examples of these geochemical relationships which are not considered in this report. Molybdenum is associated with rhenium in the primary sulfides but with vanadium, calcium, and lead in the weathered crust and in the oxygen compounds: vanadite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$; powellite, CaMoO_4 ; wulfenite, PbMoO_4 , according to Yanishevskii [19].

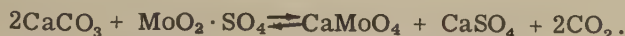
The roster of secondary minerals formed in the oxidized zone depends significantly on composition of the primary minerals of the Kadzharan. Among them we find: malachite, azurite, powellite, ferromolybdate ($\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot \text{H}_2\text{O}$), stilpnosiderite (limonite), lampadite (copper-manganese blende ore), jarosite, cuprite, halloysite, chrysocolla, and brochantite. Secondary enrichment minerals include chalcocite, covellite, and bornite.

The oxygen compounds include the mobile forms of molybdenum in supergene environments. In contrast with the abyssal primary minerals containing molybdenum chiefly in its tetravalent state, the supergene minerals yield anions of the type MoO_4^{--} , resembling CrO_4^{--} and WO_4^{--} . The resulting soluble salts (with the exception of compounds of lead) migrate easily with natural waters, penetrating joints and fissures in rocks and minerals, becoming conducive thereby to the formation of secondary minerals in the oxidized zone.

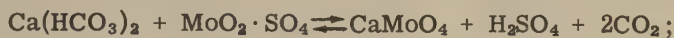
Studies by N. I. Khitarov and L. A. Ivanov [20] and by Academician S. S. Smirnov [21] had demonstrated that products of the oxidation of molybdenite may be the forms in which molybdenum is mobile in the weathered crust:



The formation of $\text{MoO}_2 \cdot \text{SO}_4$ is entirely possible in direct proximity to the sulfide ore. Acid solutions are rapidly neutralized on their contact with skarns and other rocks, many of which are limestones and dolomites, whereupon the compounds of molybdenum are subjected to substantial alteration:



Powellite and calcium sulfate are the products of this reaction. There may be also a similar reaction brought about by the prolonged contact of bicarbonate waters and molybdenite in the oxidizing environment:



A relatively stable mineral, wulfenite, PbMoO_4 , is formed naturally in the oxidized zone of polymetallic deposits where both lead and molybdenum are present. Prerequisites for the preservation of powellite and wulfenite, the secondary molybdenum minerals of the oxidized zone, were stated in the article by N. I. Khitarov and L. A. Khitarova who had demonstrated that the solubility of these minerals (powellite is more soluble than wulfenite) increases markedly at pH 1 and pH 7.5, the two extremes of the hydrogen ion levels (Fig. 2). It is shown clearly in Figure 2 that solubility of the molybdates increases abruptly on the acid side of pH 3. Solubility of both powellite and wulfenite is extremely low between pH 3 and pH 9. It begins to increase on the alkaline side of pH 9.

Assuming pH in the vicinity of 7, in the upper part of the soil-geologic profile over the molybdenum ores of Kadzharan, one might suppose that molybdenum cannot be very mobile in such environments. However, the presence of appreciable amounts of molybdenum in stream waters (0.015 to 0.031 mg per liter), in spring waters (0.31 to 0.4 mg per liter), and in mine waters (up to 1 mg per liter), as well as in soils and in plant ash (up to 0.1 mg per gram) suggests that we should be cautious in

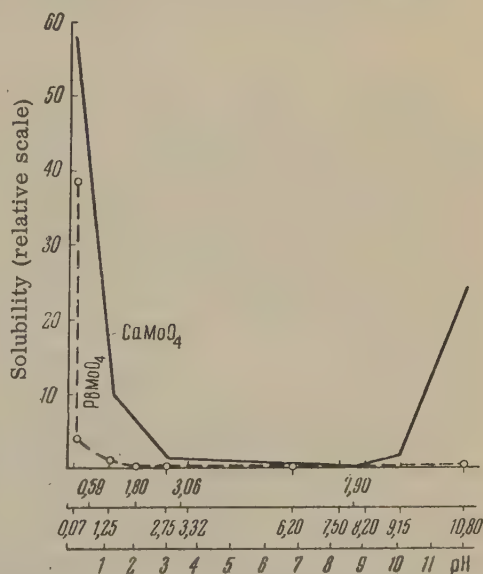
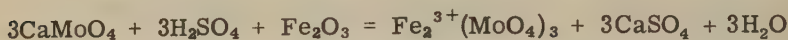


Fig. 2. Dependence of solubility of CaMoO_4 and PbMoO_4 on pH at 20° C.

any modeling of the natural processes. The effects of anions and especially of organic substance on the migration of metals are known to be appreciable indeed. Compounds of iron, copper, and soil acids need our special attention, in this respect, at the Kadzharan.

While investigating migration of molybdenum compounds in the oxidized zone, we were paying attention to the behavior of calcium molybdate, so common in molybdenum deposits. We found that a chemical reaction resulting in the formation of a fairly stable ferrimolybdate takes place on heating of a neutral solution containing molybdate and iron sulfate:



The ferrimolybdate is often related to powellite paragenetically, according to E. M. Yanishevskii [19]. The reactions here stated appear to be very common in the oxidized zone of molybdenum deposits. They are restricted, however, to the relatively acid pH. The attempts to Khitarov and Ivanov [20] to identify the ferrimolybdate in the Langar molybdenum ores, Uzbekistan, were not successful, possibly because the environments at the site they studied were not conducive to the formation of secondary minerals. As shown by the aqueous extracts, the adverse factors in question were the kind of the mobile solutes and the relatively alkaline pH (7.5).

MOLYBDENUM IN ROCKS, WATERS, SOILS, AND VEGETATION OF THE KADZHARAN DISTRICT

Molybdenum content of porphyrites and porphyry-type granites of the Kadzharan district is $1 \times 10^{-3}\%$. Monzonites contain $2 \times 10^{-3}\%$ Mo; severely altered monzonites contain $7 \times 10^{-3}\%$ Mo on the average.

In relation to the high Mo content of the rocks composing the District, there is a noticeably higher amount of dispersed molybdenum in soils, natural waters, and vegetation. Mo concentrations vary from $2 \times 10^{-3}\%$ to $3 \times 10^{-2}\%$ in soils and from $2 \times 10^{-3}\%$ to $4 \times 10^{-2}\%$ in the ash of vegetation. The results on Mo in surface and ground waters are reported in Table 3, together with the results on copper and the Cu/Mo ratios.

Table 3 shows that ground and mine waters of the Kadzharan (Mts. Pirdoudan and Yaglu-Zami) are noticeably higher in molybdenum than are waters from non-mineralized districts of Armenia. Small streams and rivers of the Kadzharan are likewise higher in molybdenum, by comparison, for example, with ordinary stream and sea waters where its content apparently does not exceed $1 \times 10^{-7}\%$ [11]. There is no doubt that the composition of the waters of a district where a reconnaissance for molybdenum is being carried on, is among the principal aids in evaluating the prospecting possibilities. Experience shows, however, that it is not easy to interpret the many metallic anomalies,

Table 3. Copper and Molybdenum in Waters of Southeastern Armenia

Water and source	% Cu	% Mo	Cu/Mo
Waters and runs, Kadzharan District	-	2×10^{-6}	-
Suboe Ozero ("Blue Lake"),			
Mt. Kaputdzhukh	6.4×10^{-7}	1.8×10^{-6}	0.35
Spring, Dzhermuk	3.0×10^{-6}	1.4×10^{-6}	2.1
and Spring, Dzhermuk	6.4×10^{-7}	1.5×10^{-6}	0.43
Spring, 500 m. N of Tunnel* 101, left			
bank of Kyz-Koshty River, Dastakert	6.2×10^{-6}	3.2×10^{-6}	2
and Narzan,** at confluence of			
Davacha and Okhchi Rivers	2.0×10^{-6}	1.25×10^{-6}	1.6
Tunnel 34, Mt. Pirdoudan	1.35×10^{-5}	5.7×10^{-5}	0.24
Spring at Tunnel* 2, Mt. Pirdoudan	2.4×10^{-5}	3.5×10^{-6}	6.8
Spring at Okhchi River Bridge,			
Mt. Pirdoudan	2.2×10^{-6}	1.8×10^{-6}	1.2
General spring at river, Mt. Davacha	2.6×10^{-5}	2.3×10^{-6}	11.3
Spring on S. slope of Mt. Yaglu-Zami			
(profile 8)	7.0×10^{-6}	7.0×10^{-6}	1.1
Spring on S. slope on Mt. Kadzharan			
(profile 16)	9.2×10^{-6}	1.2×10^{-5}	0.8
Spring at base of Mt. Ostraya (SE side)	5.8×10^{-6}	4.1×10^{-6}	1.4
Spring at base of "Mt. Orlov 12" (NE side)	-	trace	-
Tunnel 2*, Atkyz Mine	7.6×10^{-3}	5.4×10^{-6}	1400
Seepage hole, Atkyz Mine	5.5×10^{-6}	1.6×10^{-6}	3.4

Shtolnya" is translated as "tunnel." Shtolnya is a horizontal mined or excavated passage of considerable length. VPS

Narzan", in the Caucasus, is a spring containing free carbon dioxide. VPS

many metals, that may be discovered by the hydrogeologic method. In cases of this sort it is very useful to observe the ratios between the elements that are characteristic of the given kind of mineral paragenesis. Table 3 reports the Cu/Mo ratios. One may see easily that these ratios are characteristically low in waters associated with copper-molybdenum ores. The copper-molybdenum ratio in mine waters and in others is not the same as it is in the ore but is invariably 10 to 15 times as low, which is indicative of a higher mobility of molybdenum than of copper in the oxidized zone.

BIOGEOCHEMICAL ENVIRONMENT IN KADZHARAN MINING DISTRICT

The climate of the Kadzharan copper-molybdenum district is typical of the high-mountain terrains of southeastern Armenia. The mean annual precipitation is about 600 mm and is very irregularly distributed. The bulk of the precipitation is in May and June. The snow cover in winter may attain 50 cm. The mountain ranges of the Kadzharan

extend longitudinally,* with the resulting marked differences in the temperature of their southern and northern slopes and the more abundant moisture on the northern slopes [23].

The relief is dissected severely. Mt. Pirdoudan, containing the ore deposit, has very steep slopes (25 to 30°) in the north, towards the Okhchi River, and in the south towards its tributary, the Sagkar River.

The soil mantle is determined by the altitude above sea level and by the orientation of the slopes. Brown earths are common up to 1800 meters, where they are succeeded by chestnut soils (1800 to 2400 m.). The southern slopes of Mt. Pirdoudan are mantled by chestnut soils underlain by thin diluvial materials. The northern slopes are blanketed by gray mountain-forest skeletal soils. Locally, there are also chestnut soils on diluvial and proluvial-diluvial fans [24].

The southern and the southeastern slopes of Mt. Pirdoudan and the left bank of Okhchi River where the area of our prospecting interest is situated, are covered by mountain-xerophilic vegetation among which the following species are commonly found:

Astragalus aurens V. *Lagurus*;
Thymus Kotshyanus Boiss et Hoh.;
Helicrysum armeriacum;
Sedum oppositifolium Sims;
Phleum Phleclides Sims;
Thymus transcaucasicus Konn;
Dactylis glomerata L.

The following species grow extensively on old detritus:**

Hypericum perforatum;
Rumex acetosa L.;
Lapsana Communis L.;
Xeranthemum scarrosum.

The northern slopes of Mt. Pirdoudan are covered by scrub oak (*Quercus macranthera* F. et M) with the admixture of common horn-tree (*Carpinus betulus* L.), and others.*** Our work was conducted on the fairly densely forested northern slopes.

A sampling grid was set over the main part of the deposit. This grid consisted of 11 traverses (corresponding to the geologic profiles) on which soils and vegetation were taken at sampling sites 20 meters apart. The traverses were 100 to 200 meters apart. The traverses were laid out across the ore zones (veins, etc.) which are practically east-west. Width and length of the grid were 300 and 1500 meters, respectively. Approximately 250 soil samples and 300 samples of vegetation were collected. The work at Mt. Pirdoudan was begun in 1955 and continued through the summer of 1956.

*A misprint for "latitudinally", i.e. E - W (and not N - S), which is evident both from the context and the physiographic map. VPS

**In the original "mnogoletnyaya zalezh", "materials in place for many years"; the meaning is not clear. VPS

***According to N. S. Malashkina.

Soils and vegetation were analyzed spectrographically and chemically. In order to eliminate the copper interference, we used thio-*u*a (instead of SnCl_2) as the reducer of molybdenum, as proposed by B. Zaichikova [25]. The color reaction is not only unaffected by presence of copper but actually requires additions of copper, as a catalyst, in case copper is deficient, in the analysis of vegetation and soils. Iron also does not interfere with the determination and is even conducive to stability of the colored complex.

The rapid field test for molybdenum in iron- and copper-high vegetation and soils consists of the following operations:

A 0.5 gram aliquot of the soil is mixed with crystalline potassium sulfate, placed in a porcelain crucible, and fused in a muffle furnace at 500°C . The melt is taken up by heating with 10 mls of 20% hydrochloric acid, the extract is filtered, and the filtrate is made up to 15 mls (with distilled water? VPS). 5 mls of the filtrate is taken for the determination of copper. The remaining filtrate is treated with 1 ml H_2O_2 and 2 mls of 10% thiourea and the solution is shaken. After 5 minutes, 2 mls of 25% ammonium thio-cyanate is added to the solution, making the total volume of 15 mls. The contents of the cylinder are mixed thoroughly. After 20 minutes, the color is matched against standards.

As an illustration of the distribution of Mo in soils and vegetation over a known ore body in Mt. Pirdoudan, at the Kadzharan, we are reporting our findings for Profile 4, one of the 11 profiles examined (Table 4). Table 4 presents the colorimetric determinations of

Table 4. Molybdenum Content of Chestnut Soils,
Main Area, Kadzharan Deposit (profile 4) *) **)

Sample no.	Distance from entrance to Tunnel 34, meters	% Mo	Coefficient of accumulation
130	20, N., downslope	8.0×10^{-3}	26.7
128	At entrance to tunnel	6.0×10^{-3}	20.0
126	20, S., upslope	1.0×10^{-2}	33.3
124	40, S., upslope	1.0×10^{-2}	33.3
122	60, S., upslope	1.0×10^{-2}	33.3
120	80, S., upslope	1.25×10^{-2}	41.2
118	100, S., upslope	1.67×10^{-2}	56.0
116	120, S., upslope	1.66×10^{-2}	56.0
114	140, S., upslope	1.60×10^{-2}	53.0
112	160, S., upslope	1.0×10^{-2}	33.3
110	180, S., upslope	2.04×10^{-2}	68.7
108	200, S., upslope	1.5×10^{-2}	50.0
106	220, S., upslope	1.25×10^{-2}	41.2
104	240, S., upslope	8.3×10^{-3}	27.6
102	260, S., upslope	1.13×10^{-2}	37.6
100	280, S., upslope	1.02×10^{-2}	34.0

*Average Mo in soils is $3 \times 10^{-4}\%$, according to A. P. Vinogradov [12].

**I.e. % Mo divided by the Mo average (in soils). VPS

molybdenum in chestnut soils of Profile 4 of which the upper "A" horizon was sampled to the 0 - 10 cm depth.

The results in the Table show that molybdenum fluctuates from 6×10^{-3} to $2.04 \times 10^{-2}\%$, i.e. three-fold. And yet the coefficient of accumulation of molybdenum is tens of times the molybdenum average in soils (50 to 60 times). It follows, therefore, that we are still within the halo of dispersion of a molybdenum ore body.

Molybdenum content of the ash of grassy and woody plant on Mt. Pirdoudan varies from 2×10^{-3} to $2 \times 10^{-2}\%$, with the accumulation coefficient up to 20, assuming the molybdenum background of $1 \times 10^{-30}\%$ in the ash.

Molybdenum is higher in herbaceous plants than in oak leaves. At one and the same molybdenum content of the soil, $1 \times 10^{-2}\%$ (samples 100 and 112), the oak leaves contain $4.5 \times 10^{-3}\%$ Mo in the ash, as against $1.2 \times 10^{-2}\%$ in the ash of *Helicrysum arenarium*, an herbaceous composite. This relationship was supported by our later investigations. Comparisons of these findings with the geologic map of the area showed that the molybdenum "highs" in soils and vegetation may be correlated with the topography of the ore body, as a rule (Fig. 3).

In order to determine the distribution of molybdenum and copper by soil horizons of the soil-geologic profile over the mineralized zone,

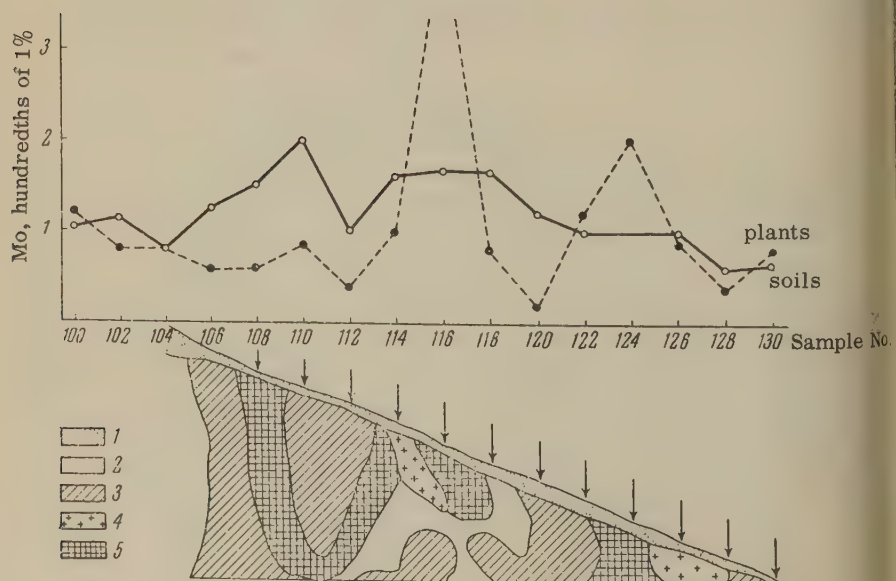


Fig. 3. Distribution of molybdenum in soil and plant ash in relation to geologic profile (Profile 4, Mt. Pirdoudan). 1—soil and diluvium; 2—unaltered monzonite; 3—weakly altered monzonite; 4—dikes; 5—mineralized monzonite.

sampled 5 profiles (traverses - VPS) to the depth of 140 cm as follows: 0 to 10 cm; 25 to 35 cm; 50 to 60 cm; 100 to 110 cm; 135 to 145 cm. The determinations of copper and molybdenum in these materials are reported in Table 5.

The results in Table 5 indicate locally high concentrations of molybdenum in the humus layer, a general tendency toward lower concentrations at 25 to 60 cm depths and an abrupt increase in molybdenum at 150 cm depth. The previously established distribution of Mo and Cu in the vertical and in the horizontal planes is confirmed also by the Pirdoudan Profile. The intermediate layer—the zone of the great development of the roots—is impoverished with respect to the elements. The occasionally observed Cu and Mo “highs” in this layer of the soil may be explained by mechanical disturbances by plowing. The localization of the higher molybdenum concentrations is related to the ore zones. In areas without any ore, the concentrations of molybdenum fall off abruptly with depth.

The downslope displacement of molybdenum peaks is not appreciable, despite the steepness of the slopes (30°). This phenomenon is explainable by the limited migration range of the molybdenum “highs” which are concentrated and firmly fixed in the humus layer of the soil in clay minerals of the eluvium.

The significant accumulations of molybdenum in soils and vegetation over the ore zone of Mt. Pirdoudan has led to a further testing of

Table 5. Distribution of Cu and Mo in Soil-Geologic Profiles, Mt. Pirdoudan

Profile	Profile, meters S. of tunnel 34	Horizon cm	% Cu	% Mo	Cu/Mo
	20 (ore-free)	0 to 10	1.1×10^{-1}	1.0×10^{-2}	11
	20 (ore-free)	25 to 35	2.4×10^{-1}	2.1×10^{-2}	11.4
	20 (ore-free)	50 to 60	2.3×10^{-1}	2.5×10^{-2}	9.2
	20 (ore-free)	100 to 110	2.4×10^{-1}	1.25×10^{-2}	20
	20 (ore-free)	135 to 145	2.8×10^{-1}	1.4×10^{-2}	20
	70 (over ore)	0 to 7	1.2×10^{-1}	1.6×10^{-2}	7.5
	70 (over ore)	25 to 35	1.4×10^{-1}	1.4×10^{-2}	10
	70 (over ore)	50 to 60	3.7×10^{-1}	7.1×10^{-2}	5.2
	70 (over ore)	100 to 110	3.3×10^{-1}	2.5×10^{-2}	13.2
	70 (over ore)	135 to 145	3.3×10^{-1}	2.8×10^{-2}	11.7
	100 (ore-free)	0 to 7	1.35×10^{-1}	1.9×10^{-2}	6.5
	100 (ore-free)	25 to 35	1.5×10^{-1}	1.7×10^{-2}	9.0
	100 (ore-free)	50 to 60	2.4×10^{-1}	2.5×10^{-2}	9.6
	100 (ore-free)	100 to 110	2.1×10^{-1}	1.7×10^{-2}	12.3
	100 (ore-free)	135 to 145	1.9×10^{-1}	1.13×10^{-2}	16.8
	150 (over ore)	0 to 7	8.5×10^{-2}	1.9×10^{-2}	4.5
	150 (over ore)	25 to 35	2.1×10^{-1}	7.1×10^{-2}	3
	150 (over ore)	50 to 60	3.6×10^{-1}	1.5×10^{-2}	24
	150 (over ore)	100 to 110	1.3×10^{-1}	1.6×10^{-2}	8
	150 (over ore)	135 to 145	2.5×10^{-1}	3.0×10^{-2}	8.1

the method in other areas. Mts. Davachi, Yaglu-Zami, and Kadzharan, on the left bank of the Okhchi River, across the river from Mt. Pirdoudan, were recommended particularly by the geologists of the Kadzharan Geologic Reconnaissance Party. The farthest of them, Mt. Davachi, is 3 km from Kadzharan Village; the others are in direct proximity of this village. Some other promising areas were also suggested: Mt. "Orlov 12", near the mining settlement of Ankavan, and Mt. Ostraya.

Prospecting possibilities of these areas were appraised by preliminary tests of waters, soils, and plants for molybdenum, using special samples collected for that purpose.

PRELIMINARY BIOGEOCHEMICAL TESTS AND SELECTION OF PROMISING AREAS

Accumulation of molybdenum in vegetation is an important criterion in prospecting for copper and molybdenum. The results from Mt. Pirdoudan showed that not all of the plant species accumulate molybdenum to the same degree. In order to investigate this phenomenon further, we sampled different plant species and their different parts (leaves, bark, wood, twigs) along Profile 4, Mt. Pirdoudan. The samples were taken in July. There were conspicuous differences in the molybdenum content of one and the same species from the mineralized and from the non-mineralized sites. Such differences were noted in leaves, bark, and woody tissue. On the whole, molybdenum tends to accumulate in leaves. There is more molybdenum in herbaceous species than in trees. Most of the herbs from one and the same site contain about the same amounts of molybdenum, as, for example, *Artemisia* spp., *Origanum communis*, *Trifolium* spp., *Potentilla* spp., *Kranz*, and others. It is possible, therefore, to use one species instead of another in the reconnaissance. Some species were found, however, that tend to accumulate more molybdenum than the others: *Gentiana*, the aurant *Astragalus*, and alfalfa.

While selecting a promising area for molybdenum, in 1956, we examined two possibilities: the left bank of the Okhchi River (Mts. Davachi, Yaglu-Zami, and Kadzharan) and Mt. "Orlov 12" at Ankavan. Orientation tests of spring waters, soils, vegetation and minerals at Mt. "Orlov 12" showed a complete absence of molybdenum, except in pyrite from a shaft; this pyrite contained hundredths and thousandths of one per cent of molybdenum.

The left bank of the Okhchi River proved to be relatively more rich in molybdenum and it was there that the biogeochemical reconnaissance was undertaken. A view of the reconnoitered terrain is shown in Figure 4.



Fig. 4. View of the left bank of Okhchi River.

PROSPECTING FOR MOLYBDENUM AT MTS. DAVACHI,
YAGLU-ZAMI, AND KADZHARAN

The entire left bank of the Okhchi River was believed to be promising with respect to molybdenum, by the geology of the Kadzharan Geologic Reconnaissance Party. This was indicated by the favorable geologic structures composed of monzonite, which is widely distributed in Pirdoudan. Moreover, molybdenum was found in spring waters on the southern slopes of Mts. Davachi, Yaglu-Zami, and Kadzharan [22]. In the summer of 1955, we covered all of the left bank of the Okhchi River by the soil-botanical biogeochemical survey, within the southern boundaries of Mts. Davachi and Yaglu-Zami. The sampling was done on the 20 x 100 meter, common rectangular grid, i.e., with the squares 100 meters apart and the sampling sites 20 meters apart. Soils were sampled in 200 gram lots of the surface horizon "A" to 10 cm depth. The fresh weight of the samples of vegetation (species only) was 100 to 150 g. each. Preliminary tests of soils and plants for Mo and Cu gave evidence of major geochemical anomalies, comparable to those of Mt. Pirdoudan. The molybdenum content of soils was up to $3 \times 10^{-2}\%$, 100 times the background.

In 1956, the adjoining area, Mt. Kadzharan, was covered by the soil-botanical geochemical survey. The soil maps of molybdenum anomalies served clearly to outline the areas of relatively high

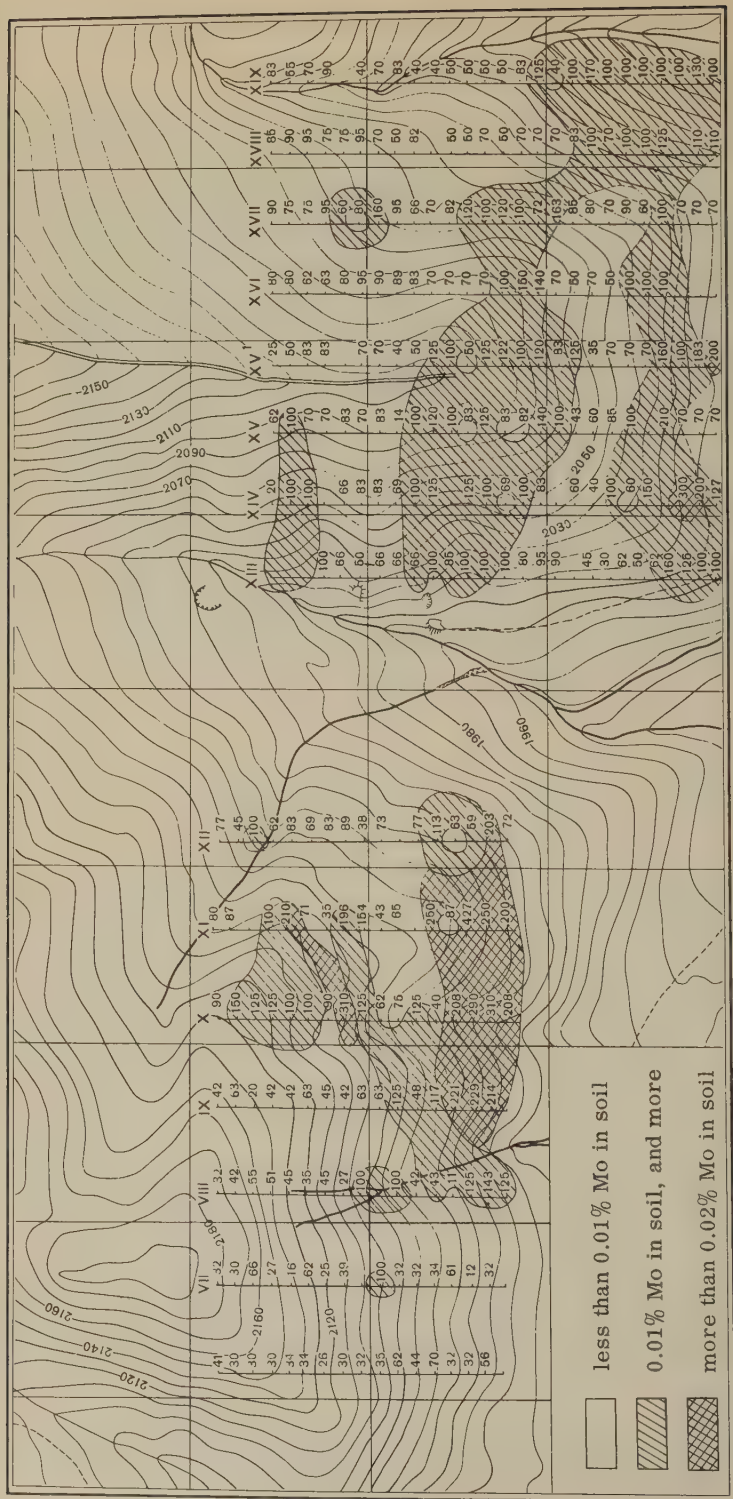


Fig. 5. Molybdenum isograds in soils of left bank of Okhchi River.

lybdenum concentrations on Mts. Davachi, Yaglu-Zami, and Kadzharan (Fig. 5).

The soil maps of molybdenum isograds for the left banks of the Davachi and Davachi Rivers were transmitted to the Kadzharan Geologic Reconnaissance Field Party for utilization in their mining-exploration project.

In 1955-1957, exploratory mine openings were made at the sites of newly discovered anomalies at Mts. Yaglu-Zami and Kadzharan. No major copper-molybdenum ore zones were found in this exploration (Tunnels 42 and 40).

Theoretically, there should be a correlation between the soil and botanical biogeochemical surveys, because of the biogenic accumulation of metals in the humus of the soil. The plant analysis data were employed, therefore, in making the botanical (biogeochemical) map, and analysis of samples taken at the same sites and on the same traverses as the soil samples: *Hypericum perforatum*, *Carum carvi*, *Urtica urbanum*, *Scrophularia*, and others. Analyses of plants from one and the same site, within the dispersion halo of the ore body, showed about the same molybdenum content, regardless of the families, in all the plant species examined. As shown in Table 6, the plant ash is richer in molybdenum, by one order of magnitude, as against the regional background (the background is $3 \times 10^{-3}\%$ Mo in the ash). The most highly enriched species are: *Scabiosa* (family *Dipsaceae*), the plant *Astragalus* (family *Leguminosae*), and *Anthriscus silvestris* (family *Umbellatae*).

The smallest amounts of molybdenum are found in *Matricaria inodora*, *Salvia officinalis*, *Chicorium intybus*, and certain other

Table 6. Mo Content of Plant Ash, Mt. Yaglu-Zami

Species	% Mo	Coefficient of accumulation
<i>Astragalus aureus</i> w	2.7×10^{-2}	27
<i>Thymus Kotschyanus</i> Boiss et Hoh.	1.8×10^{-2}	18
<i>Stachys annua</i> L.	2.7×10^{-2}	27
<i>Salvia verticillata</i> L.	1.0×10^{-2}	10
<i>Tencrium alba</i> L.	1.4×10^{-2}	14
<i>Scabiosa micrantha</i> Desv.	5.0×10^{-2}	50
<i>Scutellaria latifolia</i> L.	2.0×10^{-2}	20
<i>Teucrium alba</i> L.	1.5×10^{-2}	15
<i>Scrophularia Grossheimii</i> B. Sch.	1.2×10^{-2}	12
<i>Astrodaucus orientalis</i> Dr.	3.3×10^{-2}	33
<i>Gypsophila elegans</i> M. V.	2.0×10^{-2}	20
<i>Astragalus declinatus</i> W.	1.3×10^{-2}	13
<i>Leontodon</i> sp.	1.2×10^{-2}	12
Average	2.0×10^{-2}	20

Average in plant ash, according to Vinogradov [12], 1.1×10^{-3}

species. Despite some variations in the molybdenum content of some species, all of them, without exception, accumulate molybdenum when they grow over the ore, i.e., wherever the soils and the underlying materials are enriched by molybdenum. It becomes unimportant, therefore, what particular plant species are taken in sampling along the traverses. Where there are marked ecologic changes in the vegetation, however, it is best to sample two or three species at the site, as a precaution.

Figure 6 is a map of Mo isograds in plant ash for the left bank of the Okhchi River (Mts. Yaglu-Zami and Kadzharan). Two zones of relatively high molybdenum concentrations are plainly visible on the map, on the southeast slope of Mt. Yaglu-Zami and on Mt. Kadzharan. Both of these zones correspond closely to the anomalies shown in the biogeochemical survey of the soils. Thus both soil and botanical surveys support each other (in respect to presence, position, and size of the geochemical anomalies - VPS).

As previously stated, major ore bodies were found within the anomaly boundaries established by the surveys. These ore bodies are tens of meters thick and their area is thousands of square meters. Their outlines coincide almost exactly with the isograd maxima in the soils and in the ash ($2 \times 10^{-2} \%$ Mo). Both copper and molybdenum concentrations decrease significantly in the ore-bearing rock outside these boundaries and cease to be anomalous at a greater distance.

Comparisons of the surficial data on molybdenum in the rocks with the geologic profile in depth showed that the ore body must be situated 50 to 100 meters below the surface. It is not entirely clear so far what are the requirements for the geochemical correlations between an ore body in depth and its surficial indications. It was believed, up to this time, that the maximum depth (of ore - VPS) that may be indicated by the biogeochemical method is 20 to 30 meters and yet here, in this particular case, the depth is already hundreds of meters.

In view of the positive results of the soil-botanical geochemical survey at the Kadzharan, it was decided by the Armenian Tsvetmetrazvedka* to intensify the mining-exploration progress at Mt. Yaglu-Zami. Moreover, plans were made for the biogeochemical prospecting projects at the Dastakert (Sisian District) and at the Agarak (Mergili District).

PROSPECTING FOR MOLYBDENUM IN DASTAKERT AND AGARAK

Preliminary biogeochemical testing of the surface ground for molybdenum at the Dastakert in 1956 showed relatively high amounts

*"Tsvetnykh Metallov Razvedka" "The Reconnaissance for Colored Metals"—an administrative body in the geologic service of the Armenian SSR. VPS



Fig. 6. Molybdenum isograds in ash of vegetation, left bank of Okhchi River.

of this metal in surface and ground waters, soils, and vegetation associated with the dispersion halo of the ore body.

The Dastakert copper-molybdenum ore body is situated on the northern slopes of the Bargushat Range, at the headwaters of Kyz-Koshty River at 2300 to 2400 meters above sea level. The deposit consists of effusive rocks; porphyrites and hornfels. The ore is associated with quartz veinlets in the host rocks. The ore zones are disseminated sulfides: pyrite, chalcopyrite, molybdenite; the oxidized ores contain malachite, azurite, ferrimolybdenite, etc.

The deposit is traversed by the deep channel of the Kyz-Koshty River and is dissected by numerous gulleys with steep stony slopes. There is a tendency for many slopes to flatten out at the escarpments and at the precipitous banks of the Kyz-Koshty River channel because of accumulations of clastic materials. Thickness of the sediments may be several meters.

The soils at the deposit are predominantly mountain-meadow, chestnut, and chernozem. They were formed on the diluvium of the volcanic rocks and on the alluvial sediments.

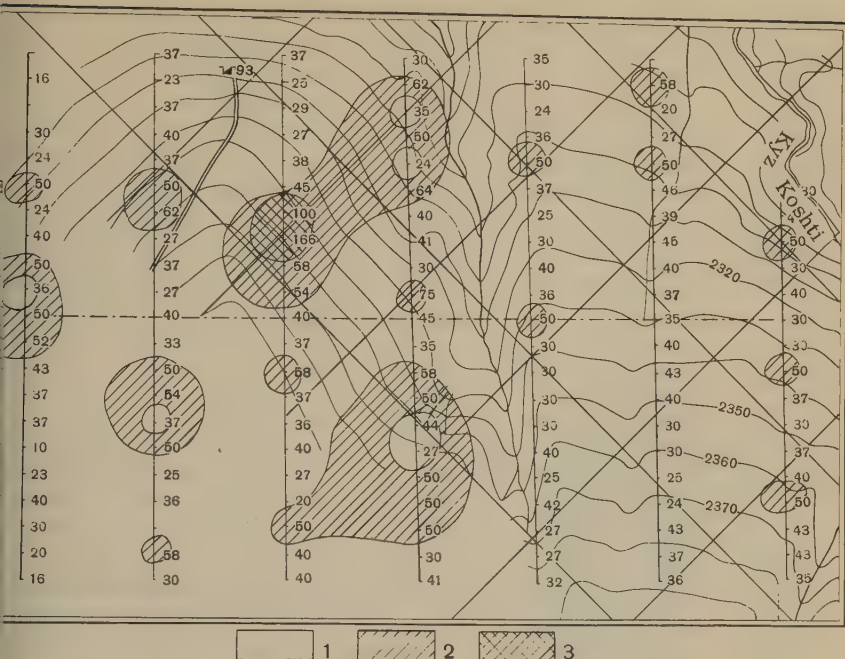
Vegetation in the zone of the deposit is of the meadow type forming a continuous blanket. A stable turf is its product, highly conducive to the conservation of the soil mantle.

Following the recommendation of N. A. Markaryan, Party Chief of the Dastakert Geologic Reconnaissance Team, we examined the southern part of the site, where geologic indications were favorable for molybdenum. Preliminary mine workings (costeans) had failed to show any mineralized zones, however, in any case. Metallometric survey had also failed to yield any positive results.

Samples of soils and vegetation were collected on 7 profiles (traverses - VPS) north to south (downslope). Length of the profiles: 400 m.; distance between the profiles: 100 m.; distance between sampling sites: 20 m. Both soils and vegetation were sampled at every site. 200 grams of soil were taken from the humus horizon "A", 0 to 10 cm. *Artragalus* species were taken preferentially among the plants. The plant samples consisted of only one species of vegetation. As a rule, 1 to 2 samples of vegetation were taken at every site, i.e. 1 or 2 plant species. Molybdenum content of soils and plant ash, as ten-thousandths of one per cent, was plotted on the 1:2000 map.

Figure 7 is a generalized map of the southern part of the area showing the molybdenum isograds in the soil. The molybdenum anomaly is conspicuous on the map. Analyses of plants (*Astragalus* spp., *Tanacetum vulgare**) from the same sites confirm the presence of the anomaly. Molybdenum content of the plant ash was up to $3 \times 10^{-2} \%$ and not below the concentrations observed over the known ore deposits of Armenia. Soils and plants were sampled on a more dense grid, toward the end of the field study of the newly discovered anomaly. The anomaly was sustained further by the analyses done in Moscow. The total

*"Pizhma"; this plant species is not mentioned elsewhere in the text of the original and not listed among the plants common in the district. VPS



7. Molybdenum isograds in soils of southern part of the Dastakert Deposit: 1—less than 0.0050% Mo in soil; 2—0.0050% Mo in soil, and more; 3—0.0100% Mo in soil, and more.

of the indicated ore body was appraised at 5000 square meters. The biogeochemical survey map was passed onto the Dastakert Geological Reconnaissance Field Team for further action. The indicated ore body will be proved by one or two tunnels from the nearest shaft. The northwestern part of the Agarak is especially promising in the reconnaissance for molybdenum.

Soils, natural waters, and vegetation were sampled by members of the Agarak Geologic Exploration Field Party, in consultation with us. The traverses were laid out, 200 meters apart, each 1 km long. Plants and vegetation (*Stachys annua*, *Carum carvi*, *terresken*) were sampled every 100 meters. The samples were sent to Kadzharan where they were examined for copper and molybdenum in the laboratory. The copper and molybdenum content of waters in the northwestern part of the Agarak was not smaller than of the waters from the mineralized areas (Mt. Pirdoudan, Mt. Yaglu-Zami). For example: Water sample No. 1— 1.2×10^{-6} % Mo; 5×10^{-6} % Cu; Water Sample No. 5— 3.8×10^{-6} % Mo; 7.5×10^{-5} % Cu. The Cu/Mo ratio varies from 2 to 4, which is the characteristic range for mine waters of the copper-molybdenum districts of Armenia.

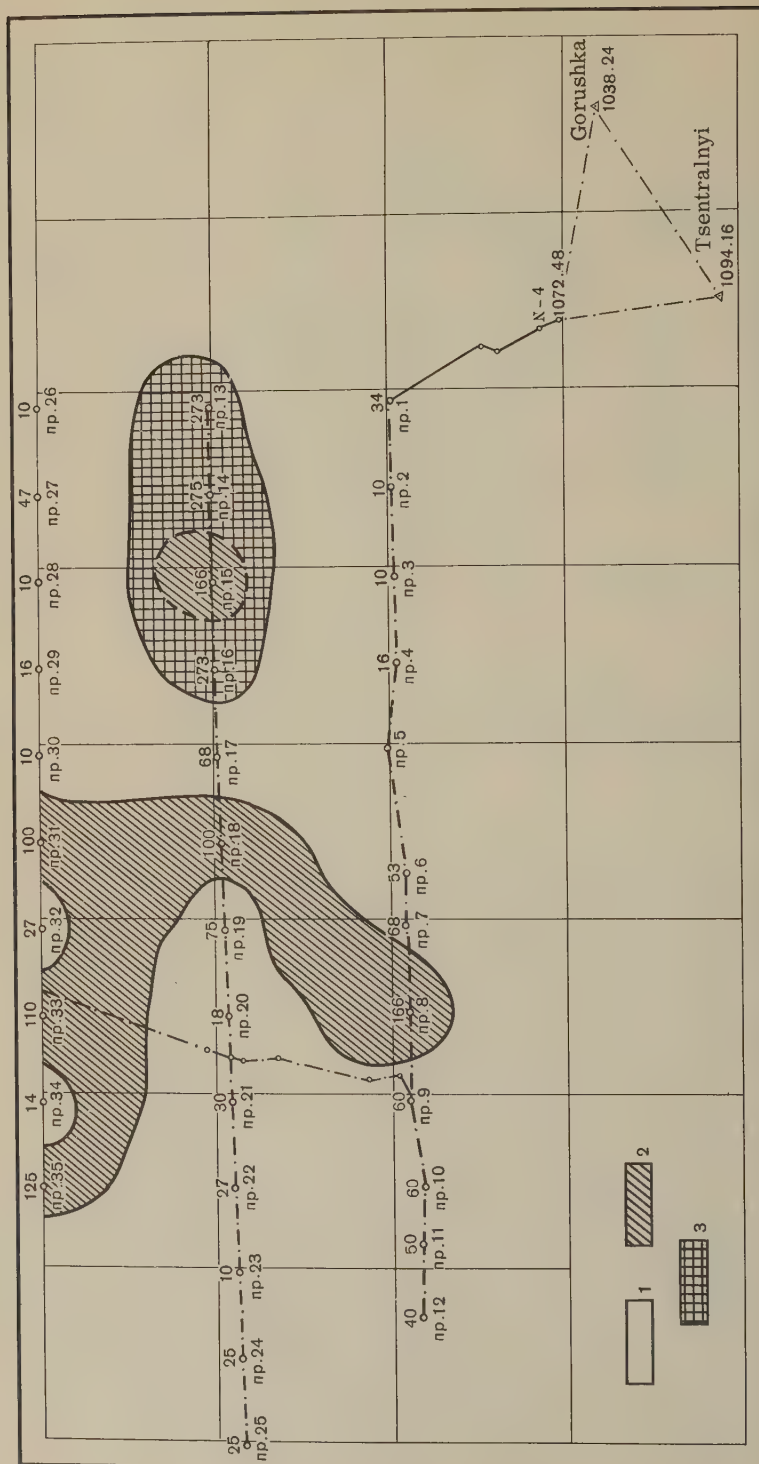


Fig. 8. Molybdenum isograds in soils of northwestern part of the Agararak Deposit. 1—less than 0.0100% Mo in soil; 2—more than 0.0100% Mo in soil; 3—0.0200% Mo in soil, and more.

Soils and vegetation proved to be definitely enriched by copper and molybdenum. Soils of the northwestern part of the Agarak have as much as $2.7 \times 10^{-2}\%$ Mo and $1.3 \times 10^{-1}\%$ Cu. Ash of the vegetation up to $3.0 \times 10^{-2}\%$ Mo and up to $1.5 \times 10^{-1}\%$ Cu. The data on molybdenum in soils were plotted on a generalized map, 1:100,000 scale, shown in Figure 8. Molybdenum anomalies (more than $10^{-2}\%$ Mo) are conspicuous on the map, against the moderate background ($3 \times 10^{-3}\%$ Mo). These results are sustained by the analysis of vegetation. The total area of the molybdenum anomalies in soils (more than 0.02% Mo) is as large as $800,000 \text{ m}^2$. The anomalies are now being tested by mining operations.

CONCLUSIONS

1. Copper-molybdenum deposits of Armenia (Kadzharan, Dastakert) can be recognized from the surface by the dispersion halos of their metallic constituents. Soils, waters, and plants in the mineralized districts are tens and hundreds of times as high in molybdenum as the average in the biosphere. A distinct copper-molybdenum biogeochemical province was established (in Armenia - VPS) by the field work engaged in the exploration.

2. Correlations between copper and molybdenum in rocks (ores), soils, and vegetation were proved in depth, by examination of geochemical profiles. These correlations are not affected by the weathering crust which extends to considerable depths or by the characteristic sediments overlying the ore. Geochemical relationships between surficial and the underlying materials are traceable for tens of meters depth.

3. Maps of molybdenum isograds in soils and vegetation made it possible to draw the boundaries of a molybdenum halo, in a promising area on the left bank of Okhchi River (Mt. Yaglu-Zami and Mt. Kadzharan). Two major ore zones were discovered, rich in both copper and molybdenum, by mining operations within the boundaries of the biogeochemical anomaly.

4. Suitability of the biogeochemical method of prospecting for copper and molybdenum was demonstrated in the Transcaucasian environments, by our work in the Armenian SSR.

5. I. Makarova, R. G. Nikitina, and N. S. Malashkina took part in the field and in the laboratory work, which is here appreciated by the author.

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HALOS OF DISPERSED MERCURY AS PROSPECTING GUIDES AT THE ACHISAI LEAD-ZINC DEPOSITS

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Abstract

Some conclusions have been made on the basis of the analysis of 4528 samples taken from various parts of the Achisai Deposit. Mercury is present in sulfide and oxidized ores in galena, sphalerite, pyrite, cerussite and smithsonite; its content in these minerals is tens and thousands times higher than its average concentration. In the rocks at a distance from the ore bodies mercury has not been detected by the method used; the sensitivity of the method is 3×10^{-5} per cent. The presence of mercury dispersion halos on the surface in the epicentres of blind ore bodies deposited at a depth of 25 to 300 metres has been established. The absence of mercury dispersion halos in the eluvium-diluvium can be explained by its dispersion, during hypogene processes, to concentrations which are below sensitivity of spectral analysis.

Sulfide and oxidized ores of the Achisai Deposit are in the Lower Carboniferous limestones and dolomites. The ore bodies are blind; they are 25 to 430 meters below the surface and they are controlled by an intricate system of tectonic breaks. In the absence of their outcrops, the following indirect indications are employed in prospecting for such ore bodies:

- a) Tectonic fractures, as shown by geophysical and geologic surveys
- b) Karst cavities, as shown by geophysical surveys (the vast majority of them are buried).
- c) Dispersion halos of lead and zinc, as outlined by metallometric surveys.

Areas containing all three of these prospecting indications are regarded as favorable for further studies. Investigations of the dispersion halos of mercury were undertaken by us in order to use them as indirect prospecting indications (of lead-zinc ores) in the environment of the Achisai Deposit.*

Mercury anomalies in ore bodies are characteristic in polymetallic deposits. The vapor pressure of mercury is much greater than of lead or zinc compounds and, therefore, mercury is far more mobile than lead or zinc in hydrothermal processes. Thus, for example, the vapor pressure of mercury is 20 mm Hg std. at 204°C, and 760 mm at 357°C; the vapor pressure of PbS is 1 mm Hg std. at 487°C [3].

*The work was done by members of the Turlan Geophysical Expedition of the Kazakh Geophysical Trust.

The vapor pressure of mercury is 800 to 1000 times as great as the vapor pressure of zinc or of lead-sulfide even at lower temperatures. Consequently, gaseous mercury is able to enter the host rocks, by way of fissures, and to spread over considerable distances, both vertically and horizontally away from the lead-zinc ores.

There is every reason accordingly to expect a development of a broad hypogene halo of mercury dispersion in the host rocks of lead-zinc ore bodies. This possibility was suggested first by A. A. Saukov [1].

Our studies of the mercury dispersion halos were conducted along the following lines:

1. Determinations of mercury in ore bodies, host rocks, and in single-mineral samples.
2. Investigations of the spread of mercury in different stratigraphic horizons of the Carboniferous and of the Devonian, in reference to distance from ore bodies.
3. Ascertaining presence of mercury in rocks over known ore bodies.
4. Testing the tectonic rupture zones of the Achisai ore field for mercury.
5. Testing of drill cores for mercury.

Mercury was determined spectrographically, with the limit of detection at $3 \times 10^{-5}\%$ [2], in 89 samples of oxidized and sulfide ores of the Achisai collected at Sites Nos. 16, 26, and 29 of the Southern Deposit and at Site No. 23 of the Northern Deposit. Mercury was found in 83 samples and could be detected only in 6 samples, at the given sensitivity of the analysis. The average mercury content for all samples was $7.9 \times 10^{-3}\%$.

Thus the mercury content of the Achisai ores is about 1000 to 1100 times the average (in the earth's crust - VPS) of $7 \times 10^{-6}\%$. The oxidized ores are noticeably enriched with mercury, with the average of $1.3 \times 10^{-2}\%$, as against the average of $6.3 \times 10^{-4}\%$ in the sulfide ores. The highest mercury, 0.1%, was found in cerussite sands, Site No. 29 of the Southern Deposit, which contain more than 60% lead.

The relationship between mercury in the host rocks and the distance from the ore body is very involved. It is important here to note that at 4 to $5 \times 10^{-5}\%$ mercury is definitely present at 140 to 195 meters distance from the ore body contact (Fig. 1). The maximum of mercury in the host rocks is up to $2.7 \times 10^{-3}\%$ (at 73 m. from the contact with the ore body).

In order to determine the "background" concentrations of mercury, we tested the rocks composing the profile of the deposit, taking samples at some distance from the known ore bodies. A profile (1400 m. long) was chosen on the northwestern flank of the Achisai ore field in which the entire section of the Lower Carboniferous limestones and dolomites was represented, including the outcrops of the Upper Devonian marl-limestones.



Fig. 1. Mercury content of host rocks crosscut 833. 1—Dolomites of the artificial horizon C, t 1-b; 2—sulfide ore; 3—tectonic fissures; 4—the Hg curve; 5—sampling sites.

Mercury was absent, by the analysis, in the 32 samples of bedrocks of the profile. Consequently the Achisai local geochemical background of mercury is outside the limit of the sensitivity of the method ($3 \times 10^{-5}\%$) and any instance of the detection of mercury in the rocks should be regarded as a true anomaly.

Determinations of mercury in single-mineral samples from the Achisai Deposit were made with the purpose of ascertaining the more definite geochemical relationships by which its presence is governed in the polymetallic ores.

It is very probable that mercury is present as an isomorphous admixture, both in the ore bodies and in the host rocks, inasmuch as there are no known mercury sulfides in the Achisai, despite the numerous mineralogic investigations by different authors.

Our studies had demonstrated the presence of mercury in all of the mineralogic varieties of the ore. The results are presented in Table 1.

The results show clearly that mercury is enriched in cerussite and that it is noticeably impoverished in smithsonite. This has a rational explanation, by reference to the well-known supergene parting of lead and zinc. The zinc ores of Achisai were re-deposited in the foot wall of the ore bodies, in the course of this process, and the migration of zinc was accompanied apparently by loss of mercury from the sphalerite in which it was originally present. Mercury accumulates therefore in cerussite ores, alongside the weakly mobile lead.

The dispersion halos of mercury were examined over the following ore bodies: No. 29, the Southern Deposit; No. 23, the Northern Deposit; the Main Deposit.

Mercury was determined in samples collected from bedrocks and loose material on the 50 by 10, and on 25 by 5 meter grid. Halos of dispersed mercury were especially clearly defined at the surface of Site No. 29, the Southern Deposit.

Table 1

Item no.	Mineral	Deposit	% Mercury
1	Galena	The Main	1 x 10 ⁻⁴
2	Galena	The Main	5 x 10 ⁻⁵
3	Galena	The Main	2 x 10 ⁻⁴
4	Galena	The Main	2 x 10 ⁻⁴
5	Galena	The Main	5 x 10 ⁻⁴
6	Cerussite	Southern 29	3 x 10 ⁻²
7	Cerussite	Southern 29	3 x 10 ⁻²
8	Cerussite	Southern 29	3 x 10 ⁻²
9	Cerussite	Southern 29	2 x 10 ⁻²
10	Cerussite	The Main	6 x 10 ⁻⁴
11	Cerussite sand	Southern 29	1 x 10 ⁻¹
12	Sphalerite	Northern 23	5 x 10 ⁻⁴
13	Sphalerite	Northern 23	6.5 x 10 ⁻⁴
14	Yellow sphalerite	Southern 28	5 x 10 ⁻⁴
15	Smithsonite	The Main	4 x 10 ⁻⁵
16	Smithsonite	The Main	7 x 10 ⁻⁵
17	Pyrite	Southern 16, Horizon 12	1 x 10 ⁻⁴

The highest mercury content in the halo at Site No. 29 was up to $1.2 \times 10^{-4}\%$; it was $1.2 \times 10^{-4}\%$ and $1.5 \times 10^{-4}\%$ over the Northern and the Main Deposits respectively.

Depth to the ore at Site No. 29 is 25 meters; depth to the ore at the Main Deposit is 20 to 30 meters; depth to the ore at the Northern Deposit Site No. 23 is 310 to 330 meters; the ore deposits are overlain by limestones.

With attention to the structural control of the ore deposition at the Bel Mazar, we tested the principal fissures and fractures* of the ore deposit, for exploration purposes, namely: the Bel Mazar and the Bel Mazar fractures and the Ekaterina, the Sidorov anomaly, and the Northern fissures. These tectonic ruptures were sampled both along their linear extent 10 to 20 meters and in profiles perpendicular to their linear extent.

Distance between the profiles was 150 to 200 meters; their length, 10 to 40 meters; distance between sampling sites, 5 to 10 meters.

The samples were taken from the bedrocks as well as from the glacial eluvial-diluvial sediments; weight of sample was 100 to 150 gms.

The tests on the Bel Mazar fracture show that mercury makes its appearance in this narrowly localized part of the fracture, east and west (Fig. 2). The Southern 29 deposit is associated with the eastern part of the fracture. The western part of the fracture is poorly mined. The highest mercury content of the fracture is $1.2 \times 10^{-4}\%$.

*"reschina" is translated as "fissure"
"razlom" is translated as "fracture." VPS

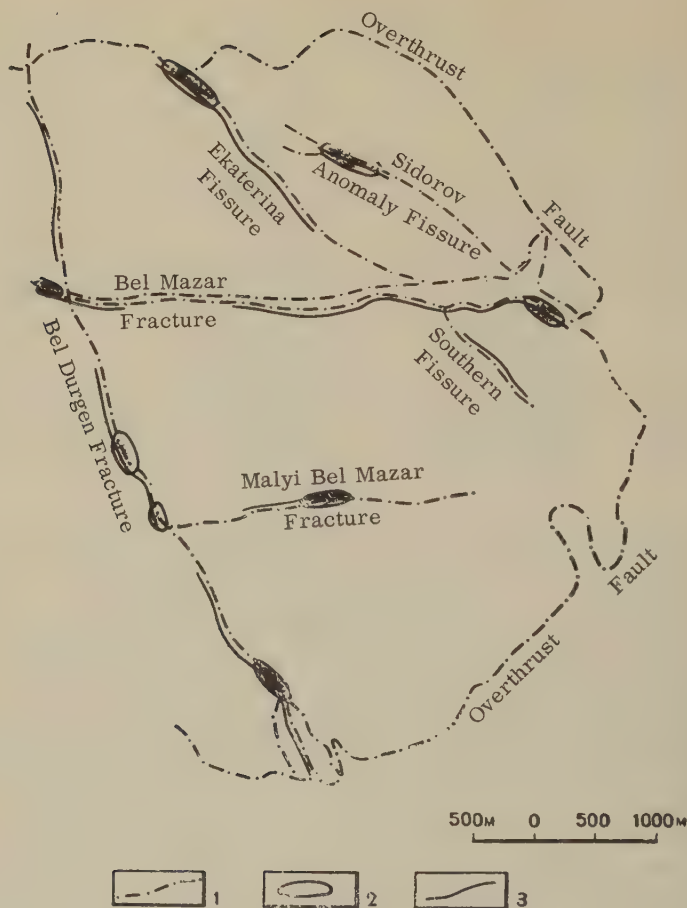


Fig. 2. Outline of principal tectonic breaks at Achisai showing sampling sites for mercury. 1—Tectonic breaks; 2—mercury halos; 3—sampling traverses.

Two halos of mercury, with the peak of $2.4 \times 10^{-4}\%$ Hg, were discovered in the Malyi Bel Mazar fracture. Three halos of mercury were discovered in the central and southern parts of the Bel Durgun fracture, with the peak of $1 \times 10^{-4}\%$ Hg. So far, no ore bodies could be found in these areas.

Along the Sidorov electric anomaly fissure, mercury halos were discovered above the epicenters of the known ore bodies. Their

mercury peaks are $1.2 \times 10^{-4}\%$ Hg. Along the Ekaterina fissure, the mercury dispersion halos were found only in its western part, with the maximum of $1.2 \times 10^{-4}\%$ Hg. No mercury halos could be found along the Southern fissure.

Drill cores were tested for mercury at every 5 to 10 meters. The results confirmed once again the presence of mercury halos over blind ore bodies. There are mercury halos in carbonate rocks at vertical distances up to 230 meters above blind ore bodies (borehole No. 2206). The results are generalized in Table 2.

Table 2

Test materials	Total number of samples	Number of samples in which Hg was not detected	Samples containing mercury		
			Number	Hg maximum	Hg %
Sulfide ore	39	5	34	4×10^{-3}	6.3×10^{-4}
Oxidized lead ore	50	1	49	1×10^{-1}	1.3×10^{-2}
Hanging walls of ore bodies (Lower Carboniferous dolomites)	90	22	68	2.7×10^{-3}	2.1×10^{-4}
Upper Devonian marl-limestones and Lower Carboniferous dolomites away from ore bodies	32	32	-	-	-
Rocks above blind ore bodies (surface):					
(a) bedrocks	460	447	13	6.5×10^{-4}	1.7×10^{-4}
(b) eluvial-diluvial materials (0.5 to 2 m. thick)	560	556	4	2×10^{-4}	1×10^{-4}
Tectonic ruptures:					
(a) bedrocks	1450	1385	65	2.5×10^{-4}	5.5×10^{-5}
(b) eluvial-diluvial materials	1730	1727	3	8×10^{-4}	4×10^{-5}
Drill cores (wall rocks)	117	112	5	4×10^{-4}	1.6×10^{-4}

CONCLUSIONS

Mercury is present in sulfide and oxidized ores and in galena, cerussite, pyrite, cerussite, and smithsonite, in amounts tens and hundreds of times as high as its average. Mercury is not detected in the Achisai rocks at a distance from the ore bodies, with the limit of detection at $3 \times 10^{-5}\%$ Hg.

2. We established the presence of mercury halos at the surface, at the epicenters of blind ore bodies which are 25 to 300 meters below the surface.

3. It was shown by testing of the principal fractures and fissures at the Achisai that mercury is present only in certain definite and narrowly localized areas of such tectonic zones.

4. In places, there are mercury halos in areas where halos of lead and zinc are entirely absent.

5. The majority of the mercury halos are fixed only in the bedrock. The absence of mercury dispersion halos in eluvial-diluvial materials may be due to a dispersion of mercury in the supergene process, to the point that its concentrations are too low to be detected spectrographically.

6. The presence of mercury dispersion halos within the boundaries of the Achisai ore field should be regarded as an indirect prospecting indication (for lead-zinc ores - VPS).

7. The mercury dispersion halos may be employed as prospecting indications of blind polymetallic ore bodies possibly also in other districts.

The foregoing conclusions are based on a large body of data represented by 4528 analyses of samples collected in different parts of the Achisai Deposit.

In conclusion, the author wishes to express his profound thanks to A. P. Solovov for his initiative and aid in the study here reported.

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ORIGIN OF NATIVE MERCURY

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Abstract

Large deposits of native mercury have been found in the Khaidarkan deposit. A number of facts indicate its hypogene genesis. These facts are: the absolute absence of signs of cinnabar leaching in nearby ore bodies, the position of mercury-bearing lenses in the overlapping shales directly above the richest cinnabar occurrences in the central part of the dome-shaped folded structure, the uniform impregnation with mercury of the surrounding shales, and the composition of admixtures in mercury which is similar to that in cinnabar from the same ore-bearing level and different from the composition of mixtures in supergene mercury.

Native mercury is a secondary mineral, as a rule, and "may be primary only in some hot springs depositing cinnabar and other sulfides, in regions of recent volcanism," according to A. G. Betekhtin.

According to A. A. Saukov [5], mercury may escape from hydrothermal solutions, in its gaseous state, because of its high vapor pressure, and may penetrate the host rocks where it may be deposited, in favorable places, as cinnabar and possibly as a finely dispersed mercury.

Native mercury is fairly common in the deposits of the South Ural mercury-antimony belt (Khaidarkan, Chauvai, Symap, Birksu, Myk, Besh-Bulak, etc.) where it forms small accumulations in isolated parts of some ore bodies, chiefly in the zones of tectonic disturbances. The supergene nature of this mercury is indicated by the numerous cavities of leaching, some of which preserve the shape of cinnabar crystals as well as fragments of cinnabar still adhering to their walls. In addition to the fragments of cinnabar, these cavities contain droplets of native mercury and fine crystals of sulfur. In addition to native mercury and sulfur, calomel may be formed also, in places, by the decomposition of cinnabar (as at the Myk and the Khaidarkan).

At the Khaidarkan mercury-antimony deposit, native mercury has been found repeatedly in several areas (the Mednaya Gora, the Main* and the Intermediate* Fields, the Kara-Acha), at rather appreciable depths (down to 200 m. below the surface). The sources of this native mercury were clusters of coarsely crystalline cinnabar, in all

Maynoe and Promezhutochnoe Pole respectively. VPS.

instances, leached by vadose waters circulating in the steeply dipping post-depositional fissures.

Large accumulations of native mercury were discovered in 1956, in the south flank of the Intermediate Field. Their depositional environments suggest a primary origin for the metal.

The main ore-bearing horizon at the Khaidarkau deposit is a sheet-like bed of quartzite (hornfels-jasperoid) breccias underlain by massive limestones of Lower and Middle Carboniferous age and overlain by Middle Carboniferous clay shales that had functioned as a semi-permeable screen. The mineralized areas (the ore fields) are controlled structurally by dome-like folds which are complicated by tectonic disturbances belonging to several systems [3, 7]. The Intermediate Field is associated with an analogous structure. Figure 1

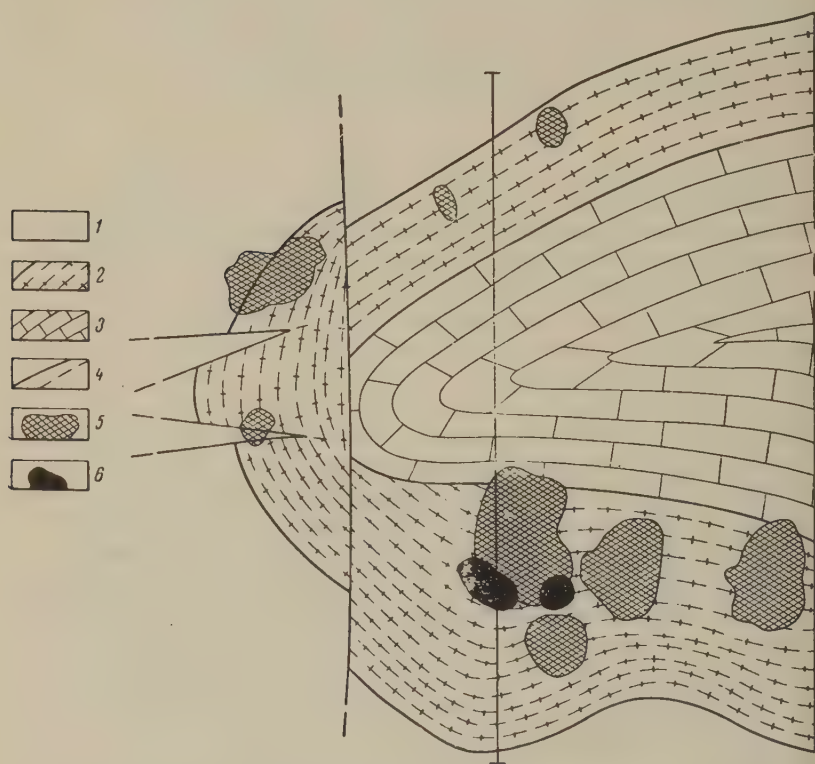


Fig. 1. Geologic structure of the western part of the intermediate field, the Khaidarkan Deposit (according to E. A. Pavlyukovich). Plan. 1—Middle Carboniferous clay shales and carbonaceous shales overlying the ore body; 2—the main ore-bearing horizon (hornfels-jasperoid breccias); 3—Middle and Lower Carboniferous massive limestones underlying the ore body; 4—tectonic ruptures; 5—high-grade clusters of cinnabar; 6—clusters of native mercury.

represents a part of the geologic section of one of the upper horizons of this field (the zone of the periclinal confinement of the dome-like ore-bearing fold). The schematic profile in Figure 2 illustrates the geologic position of a group of ore bodies in which native mercury is present.

Several large ore bodies, chiefly cinnabar, were identified within the main ore-bearing horizon (Figs. 1 and 2). The bulk of native mercury is situated higher, in the overlying shales, almost directly over the cinnabar ore bodies. Small accumulations of mercury are present in the tectonic clays. We were not able to detect any evidence whatsoever of any leaching of the cinnabar out of any of the ore bodies or out of its clusters in the lower horizons of the Intermediate Field.

The largest accumulations of native mercury were found in a small interlayer or, more exactly, a lens of carbonaceous clay shales in the sandy-clayey varieties within the zone of a small tectonic trough complicating the core of the dome-like fold (Figs. 2 and 3). This lens is associated with a tectonic "wedge" formed by two gently inclined ground triturated fissures (Fig. 4).

The overlying shales are altered considerably by the action of hydrothermal solutions whose character may be indicated by the data reported in the Table.

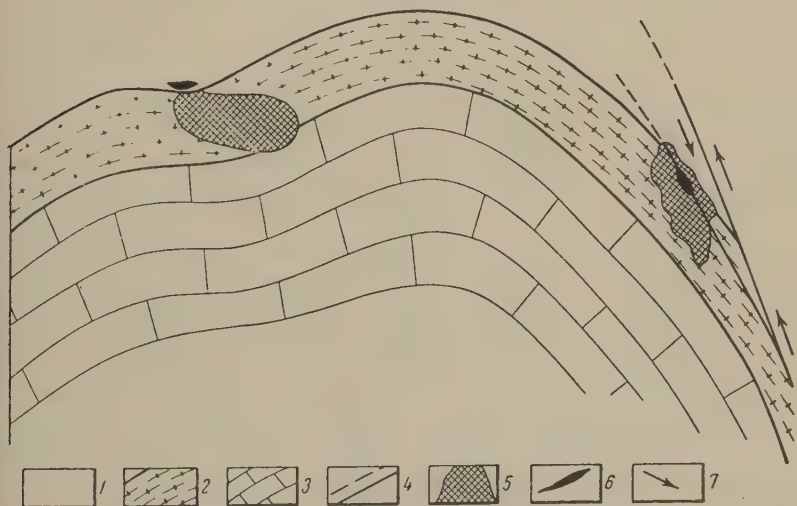


Fig. 2. Geologic structure of the western part of the Intermediate Field, the Kaidarkan deposit (according to E. A. Pavlyukovich. Profile. 1—Middle Carboniferous shales overlying the ore body; 2—main ore-bearing horizon (hornfels-jasperoid breccias); 3—Middle and Lower Carboniferous massive limestones underlying the ore body; 4—tectonic ruptures; 5—high-grade clusters of cinnabar; 6—clusters and lenses of native mercury (primary on the left, secondary on the right); 7—directions of movements along the lines of major tectonic disturbances of the upthrust-overthrust type complicated by subsequent minor movements.

The overlying shales were severely kaolinized and carbonatized in the process of their hydrothermal re-working. Concurrently, they lost some silica, some alumina, and particularly alkalis. Ferrous

Table 1. Chemical and Spectrographic Analyses of Unaltered and of Hydrothermally Altered Shales Overlying the Khaidarkan Ore Deposit*

Principal constituents	Shales overlying the ore		Carbonaceous shales with native mercury overlying the ore horizon, the Intermediate Field			
	Unaltered carbonaceous clay shales	Hydrothermally altered varieties (av. of 9 analyses)	Sample no. 1496		Sample no. 202	
			Chemical analyses, %	Recalculated on Hg-free basis, %	Chemical analysis, %	Recalculated on Hg-free basis
SiO ₂	64.90	52.80	3.80	27.50	2.74	22.57
TiO ₂	0.74	0.40	0.04	0.04	0.03	0.03
Al ₂ O ₃	12.30	11.14	0.39	2.83	0.21	1.73
Fe ₂ O ₃	1.73	4.35	0.37	2.68	0.09	0.74
FeO	3.04	0.82	-	-	-	-
MnO	0.04	0.07	trace	-	trace	-
MgO	1.47	1.54	0.00	-	0.00	-
CaO	3.19	7.61	3.14	22.75	3.00	24.59
BaO	0.10	0.11	0.17	0.17	0.09	0.09
Na ₂ O	0.85	0.36	-	-	-	-
K ₂ O	2.56	2.03	-	-	-	-
P ₂ O ₅	0.10	0.14	0.14	0.14	0.11	0.11
H ₂ O-	0.25	0.64	2.00	14.50	2.00	16.50
H ₂ O+	1.15	2.89				
Loss on ignition	6.35	9.53	91.10	43.04	93.22	49.36
CO ₂	3.13	5.86	2.36	17.10	2.46	20.80
C	2.02	?	11.44	11.44	12.06	12.06
S	0.13	1.57	-	-	-	-
SO ₃	0.91	3.08	0.85	0.85	0.78	0.78
CaF ₂	0.12	1.09	-	-	-	-
Hg	0.051	0.65	75.30	-	76.70	-
Sb	0.01	0.06	-	-	-	-
As	0.010	0.24	-	-	-	-
ZnO	0.07	0.40	-	-	-	-
Spectrographically detected	Cu,Pb,V	Cu,Pb, Ag,Sr,V	Cu,Pb,Sb, As,Sr,V, Ni,Cr	-	Cu,Pd,Ag, As,Sr,Ni	-
Sum	-	-	100.00	100.00	100.27	100.00
Vol. weight	2.64	2.64	5.35	-	4.61	-
Spec. gravity	2.71	2.74	5.40	-	5.14	-
Porosity, %	2.58	3.65	0.93	-	10.30	-

*Chemical analyses by T. T. Mukhova; spectrographic analyses by Z. M. Lopott; the Sredazsvetmetrazvedka (Central Asiatic Exploration for Colored Metals) Trust Laboratory.

oxide became converted into ferric oxide almost entirely. There is a marked increase in the amounts of carbonate. There are also accessions of some constituents from the mineralizing solutions, with the resulting formation of cinnabar, stibnite, orpiment, fluorite, sphalerite, and other minerals. The content of organic substance remains unchanged, by all appearances.

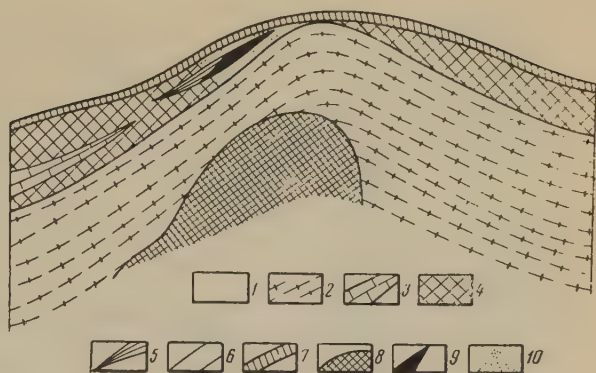


Fig. 3. Geologic position of the lens-like body of native mercury (according to M. A. Simonyan). Profile. 1—The overlying clay shales; 2—hornfels-jasperoid breccias; 3—limestone lenses in clayey-sandy shales; 4—clayey-sandy shales; 5—interlayer of carbonaceous clay shale; 6—contacts of rocks complicated by tectonic movements; 7—the gouge along inclined fissure with triturated walls; 8—a cluster of pure cinnabar; 9—native mercury (lens); 10—dispersed inclusions of native mercury.

Chemical analysis of two samples of mercury-saturated carbonaceous clay shales are reported in the Table. Their average mercury content is 76%, including 73.12 and 74.70% native mercury in sample Nos. 1496 and 202 respectively (cinnabar constitutes 2.48 and 2.39% respectively).

One may see in the microscope that droplets of native mercury, thousandths to tenths of one millimeter in diameter, are saturating uniformly the entire mass of the rock, forming particularly densely situated secretions along the inclusions of organic substances. The organic substance is seen as fine lens-like veinlets oriented parallel to the laminations of the shale (Fig. 5). The rest of the thin section consists of a colorless fine-grained aggregate, the bulk of which is quartz and calcite.

The ratio of metal reserves, as metallic mercury to cinnabar mercury, in the part of the Intermediate Field here described, is 1:4. The formation of such large amounts of metallic mercury may be explained only by the assumption of its hypogene origin. This assumption is supported by the following considerations:

a) A complete absence of evidence of any leaching of cinnabar from the ore bodies.

b) The geologic-tectonic localization. The mercury-bearing lenses and clusters are situated in the overlying shales, directly above the richest accumulations of cinnabar, in the core of the

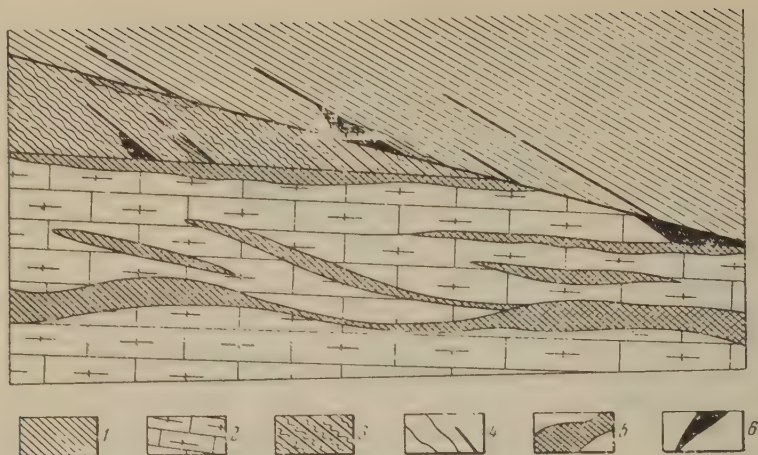


Fig. 4. Geologic positions of cluster-like accumulations of native mercury (according to E. A. Pavlyukovich). Profile: 1—Clay shales; 2—silicified finely platy limestones; 3—re-laminated carbonaceous clay shales; 4—ruptures; 5—veinlets and nests of pure cinnabar; 6—clusters of native mercury.

dome-like tectonic folds. The “wedges” formed by intersections of the gently inclined triturated fissures act like supplementary traps for metallic mercury. Mercury is intercepted most easily in the interlayers consisting of bituminous carbonaceous clay shales. Cinnabar too is accumulated more commonly in rock saturated with organic substance.

These facts are in full harmony with the ideas of A. A. Saukov. In his view, mercury passes into its gaseous state at the time of the deposition of ores. Gaseous mercury enters the overlying rocks through capillary fissures wherein it becomes precipitated in the form of extremely fine particles of cinnabar.

In the case here discussed, the concentrated solutions of ore constituents that became stagnant near the ceiling of the dome-like fold were surrounded by an especially dense mercury atmosphere. The porous shales were saturated thoroughly with mercury vapor, after they were flushed by the first portions of the hydrothermal solutions. The precipitation of mercury was favored by the impermeable screen (dense gouge) and by the relatively high proportions of bituminous substance in some isolated interlayers in the shales overlying the ore (According to Saukov, organic substance is one of the most efficient collectors of mercury from hydrothermal solutions.)

c) As to the forms of occurrence of native mercury, there is no doubt that supergene mercury accumulates in fissures and cavities, in the form of fine films and, more rarely, of small droplets. In our case, however, mercury saturates uniformly a fairly thick lens of shale in which it forms most minute droplets, adhering closely to

their host rock. Despite the very high content of mercury (average 76%), its mechanical extraction from the sample is extremely difficult.

d) The chemical composition of mercury. According to spectrographic analysis (Z. M. Popov, Analyst; the laboratory of the Nedradsvetmetrazvedka Trust), there are marked differences between supergene and hypogene native mercury in regard to their admixtures of other elements. Thus the secondary mercury collected in the zone of the post-ore disturbance, in which the Northern portion of the mineralized anticline of the Intermediate Field is

so complicated (Fig. 2), contains only traces of copper, iron, and lead. Mercury produced from the Khaidarkan ores has the same composition. Native mercury from the lens here described contains a larger number of the admixtures: antimony, lead, traces of zinc, arsenic, copper, silver (hundredths of one per cent), i.e., all of the principal constituents of the low-temperature ore-bearing solutions. The same admixtures were detected also in cinnabar which had accumulated within the main ore-bearing horizon, in the part of the Intermediate Field of the Khaidarkan here discussed.

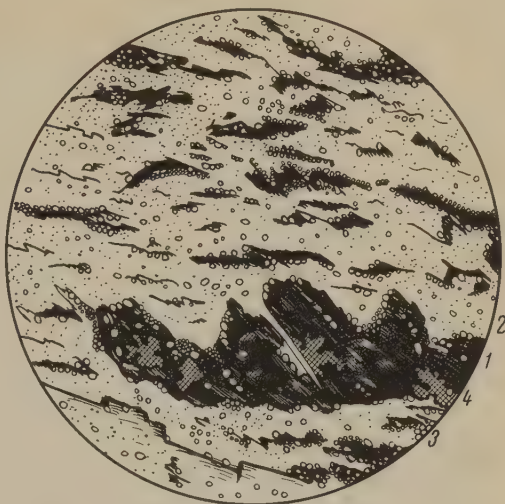


Fig. 5. Native mercury in carbonaceous clay shale. 12X. 1—Carbonaceous substance; 2—aggregates of fine-grained crystalline substance, including quartz, calcite, and kaolin; 3—the larger droplets of native mercury; 4—coarsely crystalline cinnabar.

CERTAIN PRACTICAL CONCLUSIONS

The results here reported confirm the view of A. A. Saukov [5], to the effect that mercury migrates not only in hydrothermal solutions but also in its gaseous state. Consequently, there may be two kinds of origin of mercury halos in rocks overlying the ore deposits. One kind of halo may be formed by cinnabar precipitating from residual portions of hydrothermal solutions diffusing into the overlying shales (the filtration effect). Cinnabar of such origin may be used successfully, as a micro-indicator, in prospecting for ore deposits [4].

Determinations of the cinnabar content are done by crushing of samples of the overlying rock and by panning off the heavy fraction in an ordinary pan. In the case of halos of the second kind, however, this method of determining the micro-indicator does not yield the desired result because of the finely dispersed state of mercury. Chemical analysis is more effective, by the Saukov-Aidinyan method [5], or else mercury may be determined spectrographically by the productive and very exact method developed by E. A. Sergeer and P. A. Stepanov, co-workers of the VIIR [6].

Sampling procedures are highly important. First of all, the most highly bituminous interlayers in the rocks must be sampled (the carbonaceous clay shales, aggregations of organic substance, etc.). Thus according to O. V. Vershkovskaya [2], the Khaidarkan carbonaceous shales contain 4.4×10^{-5} , and the sandy-clayey shales, $1.8 \times 10^{-5}\%$ mercury. According to our results (the average of 6000 spectrographic analyses, under the direction of P. A. Stepanov), the mercury content of the Khaidarkan bituminous shales is almost five times higher than all other rocks overlying the ore deposit, and yet their cinnabar content is three times as low as other varieties of shale, judging by the crushed samples.

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DISCUSSION

D. S. Korzhinskii's Conclusions Concerning the Phase Rule

D. S. Korzhinskii believes that the commonly accepted equation of the Phase Rule ($n = K + 2 - z$) does not express all of the characteristics of open systems with entirely mobile components, and he attempts to supplement this defect by another equation that would be applicable to such systems. However, it is not easy to agree with Korzhinskii's conclusions. Let us now recall the fundamental premises and Korzhinskii's deduction of the Phase Rule [1].

He believes that chemical potentials (or concentrations) of the entirely mobile components and the mass of the inert components should be accepted as independent parameters for open systems. Since, however, the chemical potentials are intensive and the masses are extensive parameters, he undertakes a separation of the intensive from the extensive parameters, in the equation of the Phase Rule, in order to distinguish the entirely mobile components from the inert ones.

In contrast with the commonly accepted derivation of the Phase Rule, he accepts intensive as well as extensive parameters as definitive of the equilibrium in the system.

Korzhinskii's derivation of the Phase Rule is as follows:

In a one-phase system at thermodynamic equilibrium, the parameters by which the system is defined are inter-related by equations I and II.

$$dU = TdS - PdV + \mu_1 dm_1 + \dots + \mu_k dm_k, \quad (I)$$

$$\begin{aligned} T &= \delta U / \delta S; \quad -P = \delta U / \delta V; \quad \mu_1 = \delta U / \delta m_1; \\ \dots \quad \mu_k &= \delta U / \delta m_k. \end{aligned} \quad (II)$$

where U is the internal energy; T —temperature; P —pressure; S —entropy; V —volume; $m_1 \dots m_k$ —masses of the components; $\mu_1 \dots \mu_k$ —chemical potentials of the components).

Thus $2k + 5$ parameters, $k + 3$ of which are extensive ($U, S, V, m_1 \dots m_k$) and $k + 2$ are intensive ($T, P, \mu_1 \dots \mu_k$), are inter-related by the $k + 3$ equations I and II. This serves to define the number of independent parameters. This number must be equal to $2k + 2$.

If we integrate equation I, keeping the intensive parameters constant, we obtain equation III:

$$U = TS - PV + \mu_1 m_1 + \dots + \mu_k m_k \quad (III)$$

each other, is equal to:

$$f_{\text{in}} + f_{\text{ex}} = (k + 2) r - (k + 2) (r - 1) = k + 2 \quad (\text{VIII})$$

Moreover, he calculates the maximum possible number of independent intensive parameters on the assumption that the number of such parameters in one single phase may not exceed $k + 1$:

$$f_{\text{in}}^{\text{max}} = (k + 1) r - (k + 2) (r - 1) - k + 2 - r \quad (\text{IX})$$

In general, however, the number of independent intensive parameters varies within the following limits, depending on the number of entirely mobile components:

$$0 \leq f_{\text{in}} < k + 2 - r \quad (\text{X})$$

It is not difficult to notice that equation IX, to which an independent significance is attached by Korzhinskii, is but a special case of equation X.

It may be seen from equations VIII and X that the number of independent extensive parameters may vary within the limits:

$$r \leq f_{\text{ex}} \leq k + 2 \quad (\text{XI})$$

Thus, instead of the commonly accepted equation of the Phase Rule, ($r = k + 2 - r$), Korzhinskii proposes equations VIII, X, and XI. The latter two of these, inasmuch as they are inequalities, do not fulfill the requirements of the Phase Rule. Only the first one, VIII, looks sufficiently definite, as it embraces all of the rest, and actually fulfills the function of the Phase Rule. Equation VIII is explained by Korzhinskii as follows: "The number of independent parameters in a simple system at equilibrium does not depend on the number of phases in the system and equals the number of components of the system plus two. These $k + 2$ parameters may vary independently of each other, while all of the remaining parameters vary in dependence on them" [1, p. 8]. Consequently, we are dealing with a phase rule without any phases. This alone is sufficient to put us on guard, when it comes to Korzhinskii's conclusions.

Even such an important concept as "the number of degrees of freedom" loses its definite character with Korzhinskii. Ordinarily, "the number of degrees of freedom" is understood as the number of parameters which may be changed at will, without affecting the number of phases in a system at equilibrium, with the understanding that temperature, pressure, and concentration of components (the chemical potentials) are the parameters. We find the following definition in Korzhinskii: "By the number of degrees of freedom" in the Phase Rule is meant the maximum number of intensive parameters that may vary independently, provided the state of the system does not depend on extensive factors. In real systems, only part of these intensive parameters are actually independent, i.e., only part of them function

as "the factors of equilibrium," while the rest are subject to variation depending on variations of the extensive factors of equilibrium [1, p. 12].

Korzhinskii corrects the foregoing definition of "the number of degrees of freedom" in his latest publication [2], but, as before, in his derivation of the Phase Rule, he obtains the equation $f_{in} + f_{ex} = k + 2$ alongside $n = f_{in}^{max} = k = 2 - z$.

Let us make two comments on the ideas of Korzhinskii:

A) In derivation of the Phase Rule, only intensive parameters are taken as independent. This is done for the following reasons:

First, equilibrium does not depend on size of the phases. For example, in a "water-vapor" system at equilibrium, if we double the volume of either water or vapor while the pressure and the temperature remain unchanged, the equilibrium will not be disturbed. Consequently, a simple change in the size of the phases is not considered in the derivation of the Phase Rule. Gibbs, in particular, pointed this out in his definition of phases: "In considering the different homogeneous bodies which can be formed out of any set of component substances, it will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies as differ in composition or state different *phases* of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase" [3, p. 96]. In contrast with intensive parameters, extensive parameters are determined by the size of the phase. Consequently, it is the intensive and not the extensive parameters that are employed in the derivation of the Phase Rule.

Secondly, the phase equilibria are defined by equations VII which contain only intensive parameters. This is the second reason why only intensive parameters are employed in the derivation of the Phase Rule.

Korzhinskii's choice of extensive parameters as being independent, alongside intensive ones, cannot be regarded therefore as fortunate.

Korzhinskii says: "Components whose masses or mols are factors in the system's equilibrium may be called immobile" [2, p. 19]. This is objectionable, since the equilibrium of the system is not determined by masses of its components. The chemical potentials are the equilibrium factors, in the instance of immobile as well as of entirely mobile components. Chemical potentials of the components should be regarded as independent variables and the masses as their functions, in the analysis of a system from the point of view of its equilibrium.

Choice of the independent variables depends, in many respects, on the statement of the problem. If, for example, the system is examined with respect to external conditions affecting the system, it is convenient to employ chemical potentials as independent variables, for some of the components (the entirely mobile ones), and to employ masses for some others (the inert ones), as is done by Korzhinskii. In this particular case, masses of the inert components will be independent variables with respect to their chemical potentials but will not be the equilibrium factors.

B) Our second comment refers to Korzhinskii's use of equation I. Gibbs uses equation IV, in his derivation of the Phase Rule, inasmuch as it does not involve any changes in the size of the phases. Korzhinskii uses equation I which, in contrast with IV, involves changes in the size of the phases. Gibbs says: "We know, however, *a priori*, that if the quantity of any homogeneous mass containing n independently variable components varies and not its nature or state, the quantities $U, S, V, m_1, m_2, \dots, m_n$ will all vary in the same proportion" [3, p. 86]. Consequently, in order to exclude from our consideration the size of the phase, it is sufficient to assume constancy of one of the intensive parameters here enumerated. Then the number of independent variables in equation I will be the same as in equation IV, namely, $k + 1$. Hence the number of independent variations in a multiphase system will be $k + 2 - r$.

Thus it may be easily seen that the equation $f_{in} + f_{ex} = k + 2$ differs in its meaning from the meaning assigned to it by Korzhinskii. Korzhinskii proposed a good formulation of the "mineralogic Phase Rule" in 1936 [4, p. 45]:

"In a general case, the maximum number of stable minerals that may be formed in a rock at the same time equals the number of components of the rock minus the number of entirely mobile components and of components whose concentrations in all of the minerals are below the limit" or "minus the number of the entirely mobile components and the number of the admixtures," where the entirely mobile components are those whose concentrations are determined by external factors. Concentrations of the "admixtures" are arbitrary. The supplements to the Phase Rule introduced by Korzhinskii in 1949 are not particularly fortunate.

In conclusion, I wish to give my thanks to I. R. Krichevskii, Doctor of Chemical Sciences, who called my attention to the works of Gibbs and to A. S. Pavlenko and A. I. Tugarinov, Candidates of Geological-Mineralogic Sciences, for their suggestions in the preparation of this article. I am especially indebted to D. S. Korzhinskii, who became acquainted with my questions and who answered them in detail. Unfortunately, it is difficult to agree with some of his theses.

I. V. Alexandrov

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THE STATISTICAL METHOD OF DETERMINING THE HOMOGENIZATION TEMPERATURE OF LIQUID INCLUSIONS

Measurements of the Temperature of
Crystallization of Quartz from Solutions

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Abstract

The authors apply the law of large numbers to the interpretation of the data obtained from numerous determinations of apparent temperature; they have utilized the method of homogenization of liquid-gas phases of the inclusions from the quartz crystals of various occurrences. The histograms and the frequency curves represented give the possibility to appreciate the frequency maxima and the variation limits of the crystallization temperature in the same quartz crystal or in different points of the same deposit; they permit also some conclusions about the geothermal gradient of the ascending hydrothermal solutions.

Among the many methods on record of determining the temperatures at which rocks and minerals are formed, there is the method of the homogenization of the gas-liquid phases that may be present, as inclusions, as in quartz. This method, here to be described, has been studied in its greatest detail by numerous authors, including many famous Soviet scientists. Thus G. G. Lemlein [1] cites more than one hundred papers devoted to this method.

There have been critical investigations with the purpose of testing the suitability of this method. E. I. Vulchin [2], in his studies of various heterogeneous systems resembling, in their composition, liquid inclusions in minerals, concluded that the homogenization method is suited only to systems whose pressures and temperatures are not particularly high. We may accept the critical temperature of water as the upper limit.

The authors of the present article had measured the temperatures for different parts of transparent quartz crystals of different origin [3, 4, 5].

The sample is heated gradually in a paraffin oil bath. The oil is heated electrically, so as to raise its temperature up to 70°C, and at a rate of 0.5°C per minute near the homogenization temperature.

It was possible to observe experimentally that the homogenization temperature varies within a definite range for one and the same

crystal. For example, a crystal of quartz from Nikulitel (Northern Dobrudzha, Rumania) had a range from 94 to 115°C; another crystal, from 103 to 126°C, etc. These facts indicate that there are differences in the degree to which the cavities in the quartz crystal are filled and, consequently, that the cavities were formed in a changing environment. Some of the variations in the environment were accidental, whereas some of its other aspects were essentially constant.

In order to eliminate the accidental factors, we applied the principle of large numbers, in relation to the fairly large number of our measurements of the homogenization temperatures.

Table 1 reports the homogenization temperatures for inclusions in crystals of secondary quartz taken from several fissures in quartz sandstone in the open cut of the Dervent Malkochi Hill, Northern Dobrudzha. The sandstone is believed to be Verfenian.*

The results in Table 1 show that there are appreciable differences in the individual measurements of the homogenization temperature. It follows, therefore, that there is no consistency in these measurements and the method** is not suited for the purpose.

If, however, the homogenization temperatures are treated statistically, the resulting histogram becomes a curve, quite regular in the frequency distribution and also symmetrical in its two arms (Fig. 1). One may assume, under the circumstances, that the arms of this curve represent concrete examples of the predominance of accidental factors during crystallization, whereas the maximum frequencies represent ordinary conditions. The arithmetical mean for the homogenization temperature of the inclusions in the Malkochi crystals is: $M_{104} = 136.8^{\circ}\text{C}$; it corresponds to the temperatures characteristic of the maximum frequency of the results.

We should mention also that Grushkin [6] constructed analogous diagrams for fluor spar, on the basis of numerous determinations of the homogenization temperature. He points out that individual measurements of the temperature give only relative results in appraisals of the depth at which the given deposit was formed.

The second example chosen by us is the quartz veins cutting through diabase rocks of subaqueous origin (Nikulitel, Northern Dobrudzha). This diabase is Middle Triassic in age.

We examined crystals from the following veins at the Nikulitel: a) The Main Vein, Tugulea Hill; b) The Eastern Group; c) Vein 1, Dealul din Miilek Hill; and d) Vein 2, Dealul din Miilek Hill.

The diagram for the main vein of the Tugulea Hill shows that the homogenization temperatures range from 90 to 130°C (Fig. 2). The temperature curve is asymmetric, with the highest frequency between 110 and 120°C, and with the arithmetical average somewhat less than

*"Verfenian" is synonymous with "Scythian" which is the lowermost division of the Triassic. VPS

**I. e., that any single measurement of the homogenization temperature means very little by itself. VPS

Table 1. Dervent Stone Open Cut Quarry - Mal'Kochi

Item no.	Crystal no.	Diam. of gaseous bubble mm	Homogeni- zation temp. °C	Item no.	Crystal no.	Diam. of gaseous bubble mm	Homogeni- zation temp. °C
1	11	0.01	128	53	5	0.01	135
2	11	0.02	133	54	5	0.02	130
3	11	0.01	128	55	6	0.01	130
4	11	0.02	135	56	6	0.02	147
5	11	0.02	140	57	6	0.01	135
6	12	0.02	143	58	6	0.01	149
7	12	0.01	138	59	6	0.02	140
8	12	0.02	141	60	6	0.01	152
9	12	0.01	132	61	6	0.01	145
10	12	0.01	139	62	6	0.01	138
11	12	0.02	140	63	6	0.01	134
12	12	0.01	134	64	7	0.01	140
13	13	0.01	139	65	8	0.01	136
14	13	0.01	136	66	8	0.01	145
15	13	0.01	133	67	8	0.01	129
16	13	0.01	134	68	8	0.02	146
17	13	0.02	136	69	8	0.01	140
18	13	0.02	129	70	8	0.01	134
19	13	0.01	143	71	8	0.01	136
20	13	0.01	144	72	8	0.01	146
21	1	0.02	142	73	8	0.01	137
22	1	0.01	133	74	8	0.01	147
23	1	0.01	130	75	8	0.02	148
24	1	0.02	140	76	8	0.01	145
25	1	0.01	135	77	8	0.01	143
26	1	0.01	137	78	8	0.01	138
27	1	0.02	145	79	8	0.01	135
28	1	0.02	141	80	8	0.01	128
29	1	0.01	132	81	8	0.01	137
30	1	0.01	139	82	9	0.02	140
31	2	0.01	135	83	9	0.01	127
32	2	0.01	133	84	9	0.01	139
33	2	0.01	127	85	9	0.01	143
34	2	0.01	130	86	9	0.01	133
35	2	0.01	142	87	9	0.01	135
36	2	0.01	135	88	9	0.01	138
37	2	0.01	140	89	9	0.02	145
38	2	0.01	136	90	9	0.01	131
39	3	0.01	134	91	9	0.01	127
40	3	0.01	130	92	9	0.01	138
41	3	0.02	140	93	9	0.01	135
42	4	0.01	130	94	9	0.01	140
43	4	0.01	127	95	9	0.01	124
44	4	0.01	136	96	9	0.01	137
45	4	0.01	140	97	9	0.01	136
46	5	0.01	132	98	9	0.01	129
47	5	0.01	127	99	9	0.02	139
48	5	0.09	134	100	9	0.01	128
49	5	0.01	138	101	9	0.01	124
50	5	0.02	141	102	10	0.01	135
51	5	0.01	145	103	10	0.02	143
52	5	0.02	143	104	10	0.01	147

Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of *Geochimica et Cosmochimica Acta*, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U.S.S.R., there have come into being a variety of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made. It is hoped that there will be sufficient interest in this journal to justify translation and publication (as complete volumes) of the issues for 1957 and 1956. If individuals and organizations who would purchase such translations will write to one of the Editors, the work will be undertaken when enough expressions of interest have been received to justify the expense involved. Prices presumably would be approximately the same as for the 1958 issues.

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Translation Editor

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